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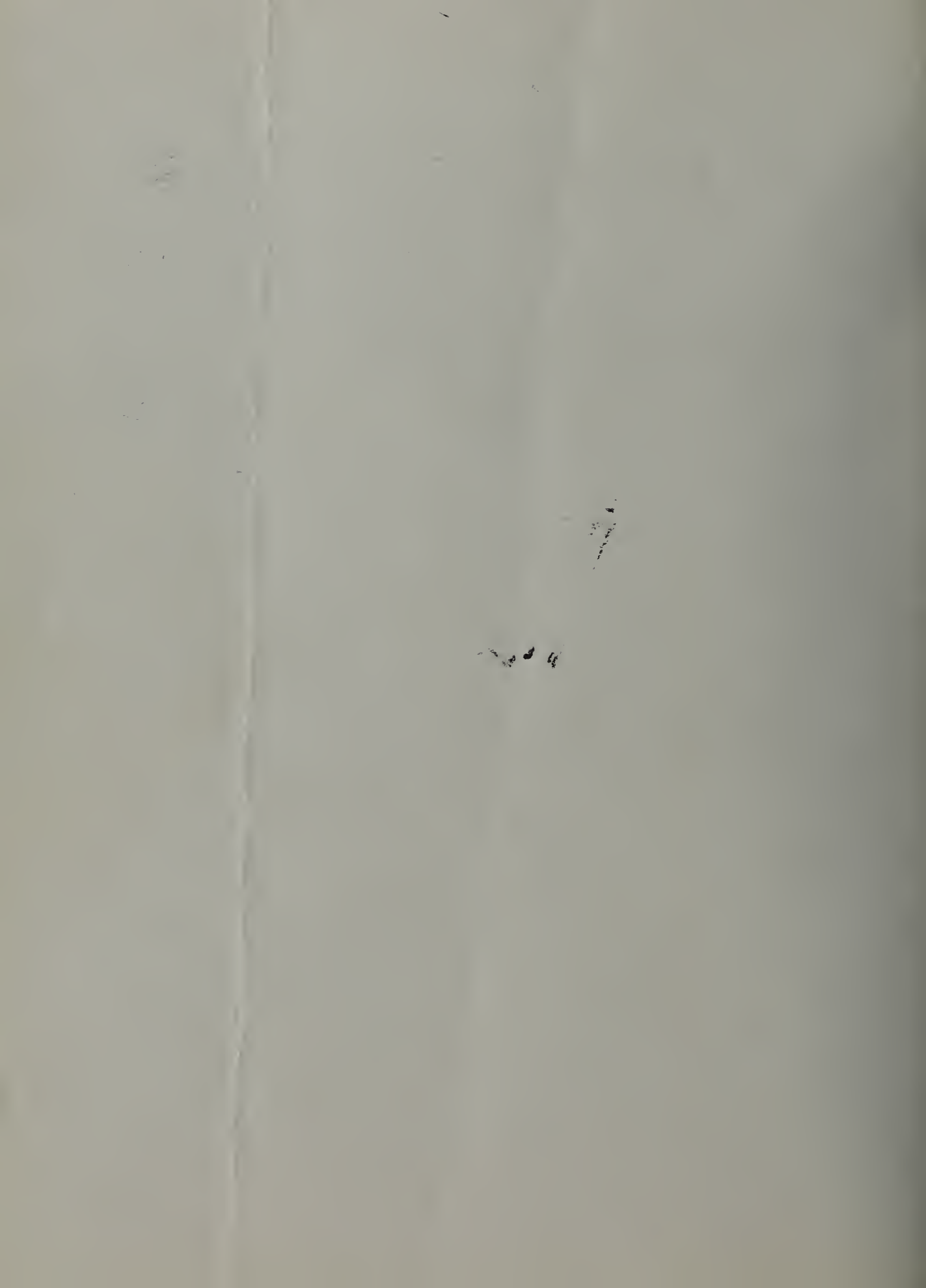
CIVIL ENGINEERING STUDIES

SANITARY ENGINEERING SERIES NO. 9
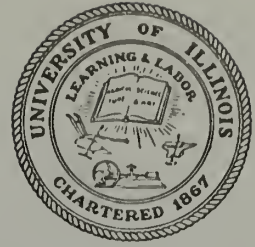
FUNDAMENTAL FACTORS IN TREATMENT
OF IRON BEARING WATERS

By

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First Progress Report on Project RG-6436
February 1959 to December 1960

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OF IRON BEARING WATERS

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January 10, 1961

SUMMARY

A pilot-scale treatment plant, consisting of a storage reservoir, diffused air aerator, reaction-sedimentation unit, and rapid sand filter, has been used to investigate the fundamental factors governing the treatment of iron-bearing waters. A satisfactory procedure for synthesizing waters containing known components has been developed, including a method of maintaining iron in the reduced state to simulate natural waters.

Twenty-four pilot plant studies have been completed. Waters studied included 10 synthetic waters, 8 natural waters studied in the laboratory, and 6 natural waters studied in the field. The waters selected for investigation varied with respect to concentrations of ammonia, sulfate, hardness, alkalinity, and iron. The overall removal of iron by the pilot-plant, regardless of water composition, has been satisfactory with one exception. Bench-scale studies have indicated some difficulty in iron removal by usual processes when a dicarboxylic acid was present. In the pilot plant, the aerator unit, which consistently increased the DO to about 80 per cent of saturation, was found to remove approximately 25 per cent of the iron, the reaction-sedimentation unit about 3 per cent, while the filter removed from 90 to 100 per cent of the iron applied to it. A greater rate of oxidation of iron appeared to occur in the filter as opposed to that in the aerator and reaction-sedimentation unit. The detention time in the reaction-sedimentation unit was found to have no effect on overall iron removal. High sulfate concentrations apparently improved removal of iron by the reaction-sedimentation unit. Concentrations of alkalinity when in excess of the hardness of a water enhanced ferrous iron oxidation.

Little correlation to date has been found between COD, organic nitrogen and iron removal efficiency. It should be noted, however, that COD values as high as 52 mg/l have been found in natural waters. ORP measurements made to date have shown only that raw waters with a negative value change to a positive value as a result of treatment.

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I INTRODUCTION

A. Nature and Importance of the Problem

The undesirable presence of dissolved iron in potable or industrial process water supplies has been recognized for a very long time. The first treatment of a water supply for the removal of iron was made in Germany in 1868. Since that time, much has been learned regarding the nature of the existing forms of iron in raw water, and several satisfactory treatment techniques have been developed.

As far as is known, however, the fundamental principles of iron removal and their relationships to the small concentrations of seldom evaluated, but important, constituents of a water are not understood to a degree which permits the design of a facility with any assurance of satisfactory iron removal. In fact, the variations in waters which seem to make the difference between a successful or an unsuccessful application of a treatment process are not usually included in a routine mineral analysis of a water. The result is that most iron removal plants are designed on the basis of an existing plant which is successfully treating water of a similar mineral characteristic. Proposed treatment methods are only occasionally tried on a pilot plant scale. An extensive literature survey made in association with the current research project has confirmed these observations.

The problem of iron in water supplies is world wide, but varies considerably in magnitude. In the United States, and particularly in the central states, where deep wells are the source of water for many communities, the problem is especially acute. For example, 70 per cent of the public water supplies in Illinois contain iron in excess of the U. S. Public Health Service limit of 0.3 mg/l. Current data indicates that one-third of these plants having iron removal facilities are not reducing the iron content of the finished water to a satisfactory level.

B. Iron Removal Methods

The removal of iron from water can be accomplished by the following methods:

    a. Conversion of soluble iron compounds to insoluble forms, followed by removal of the insoluble material.

    b. Removal by ion exchange.

    c. Conversion of soluble iron compounds to insoluble forms by oxidation utilizing an ion exchange resin especially treated to possess oxidized ions at the exchange sites. (This is the so-called Manganese Zeolite.)

    d. Removal by the conventional lime-soda ash softening process.

    e. Combinations of the above.

The method being investigated to date in this study is that of oxidizing the soluble iron forms in the water to insoluble forms by aeration and removing these insoluble forms from the water by sedimentation and rapid sand filtration.

Oxidation of the ferrous forms present in natural waters is usually accomplished by aeration; however, in the case of waters containing organic matter which form interfering colloids with the iron, all the iron is not readily oxidized by aeration. To date, the nature of this interference is not fully understood.

II EXPERIMENTAL EQUIPMENT AND PROCEDURES

A. Pilot Plant Equipment

The pilot plant equipment used in this study was designed as an integrated series of unit processes. This approach was taken to provide flexibility in operation and to facilitate modification of the treatment processes when applied to waters of widely varying mineral character.

Rubber, glass and transparent rigid plastics ("Lucite" and "Plexiglas" trade names) were used throughout the apparatus to insure that results would not be influenced by the pick up of iron from the equipment. The water being studied does not contact any metal during the treatment process, and care was taken to avoid the use of ferrous accessories where rust or corrosion products could fall into any water during operation or sampling.

The entire apparatus was made so that it could be easily disassembled and transported for field studies. Figure 1 is a photograph of the pilot plant set up in the laboratory.

The units built for the initial study of removal of iron by aeration, sedimentation, and filtration were a) a feed tank and constant head flow regulator, b) aerator, c) reaction-sedimentation unit, and d) a rapid sand filter.

Figure 2 is a line drawing of the assembled units.

For field studies, an overflow stand pipe to provide a constant head was substituted for the feed tank and constant head device.

Necessary stands, supports and accessories position the equipment for a gravity flow through the plant from the elevated feed tank or the overflow stand pipe. No pumping was necessary for laboratory studies; for field studies, the municipal utility's well pump was used to feed the overflow stand pipe.

Figure 3 is a photograph of the unit in the field.

The feed tank and constant head flow regulator are diagramed in Figure 4. The feed tank also served as a mixing vessel when synthetic waters were used. A device with six sintered glass diffusers connected to a manifold and common supply pipe served to introduce nitrogen for oxygen stripping, CO_2 to facilitate solution of carbonates, and for mixing.

The aerator is a multiple pass, diffused air unit with the water introduced under gravity pressure. The water leaves via an overflow weir and collection channel. The unit is diagramed in Figure 5. Air is introduced through a grade M sintered glass diffuser 30 mm in diameter. The combination of the velocity of the water leaving the jet and the lighter density of the water and air bubble mixture causes a vertical current within the small central tube which
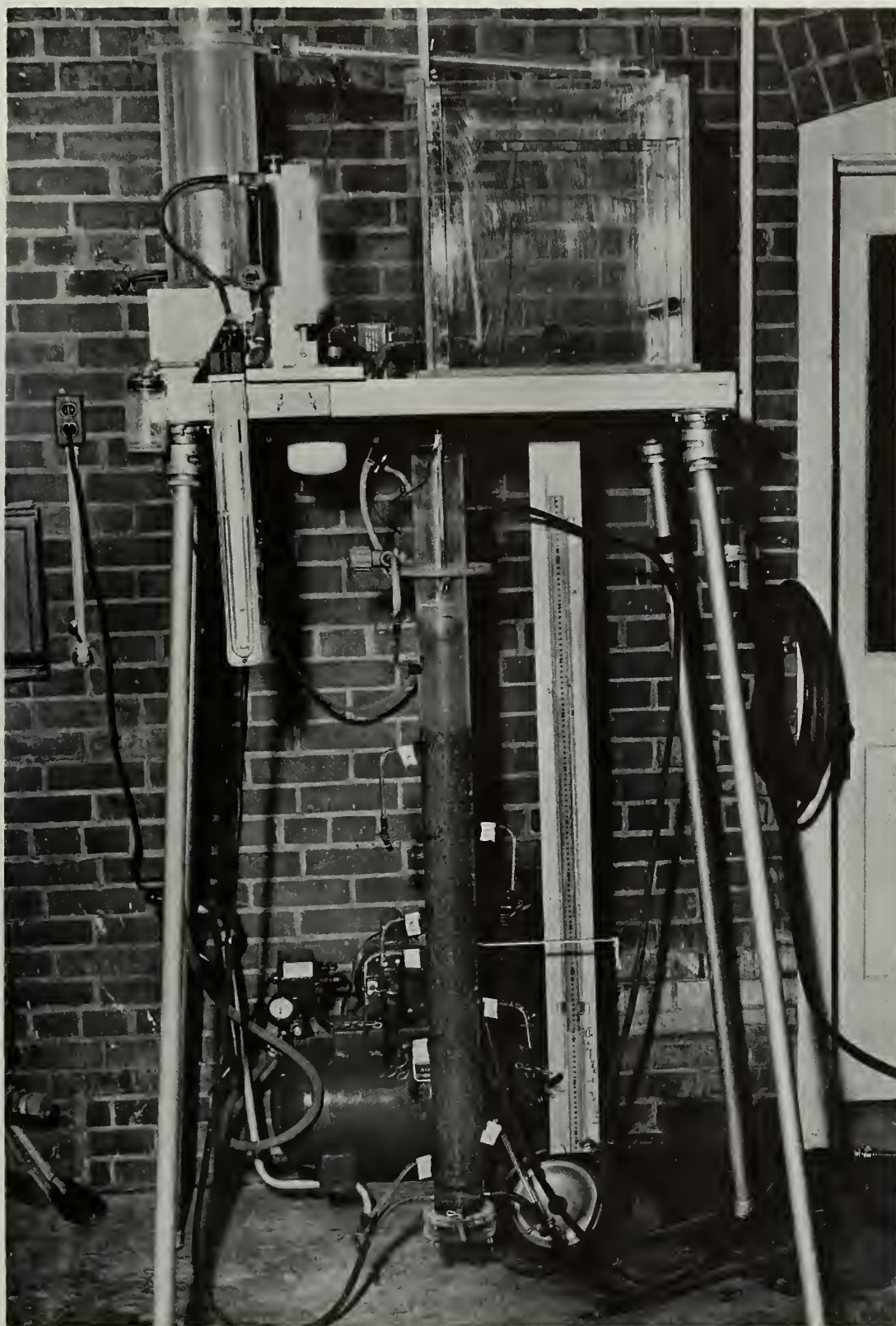
FIGURE 1

The Pilot Plant as Set Up for Laboratory Studies

ELEVATION
INCHES
191
MAX — HEAD TANK

153.5 — TABLE & SUPPORTS

CONSTANT HEAD DEVICE

135

120.5 TOP OF SECOND FLOOR

A RAW SAMPLE TAP
B AERATED SAMPLE TAP
C SETTLED SAMPLE TAP
D FINISHED SAMPLE TAP

AERATOR REACTION TANK

88

B

A

66

AIR IN

C

FILTER

FILTER
SAMPLE
TAPS

D

0 FIRST FLOOR

DRAIN

FIGURE 2

LINE DRAWING OF PILOT PLANT
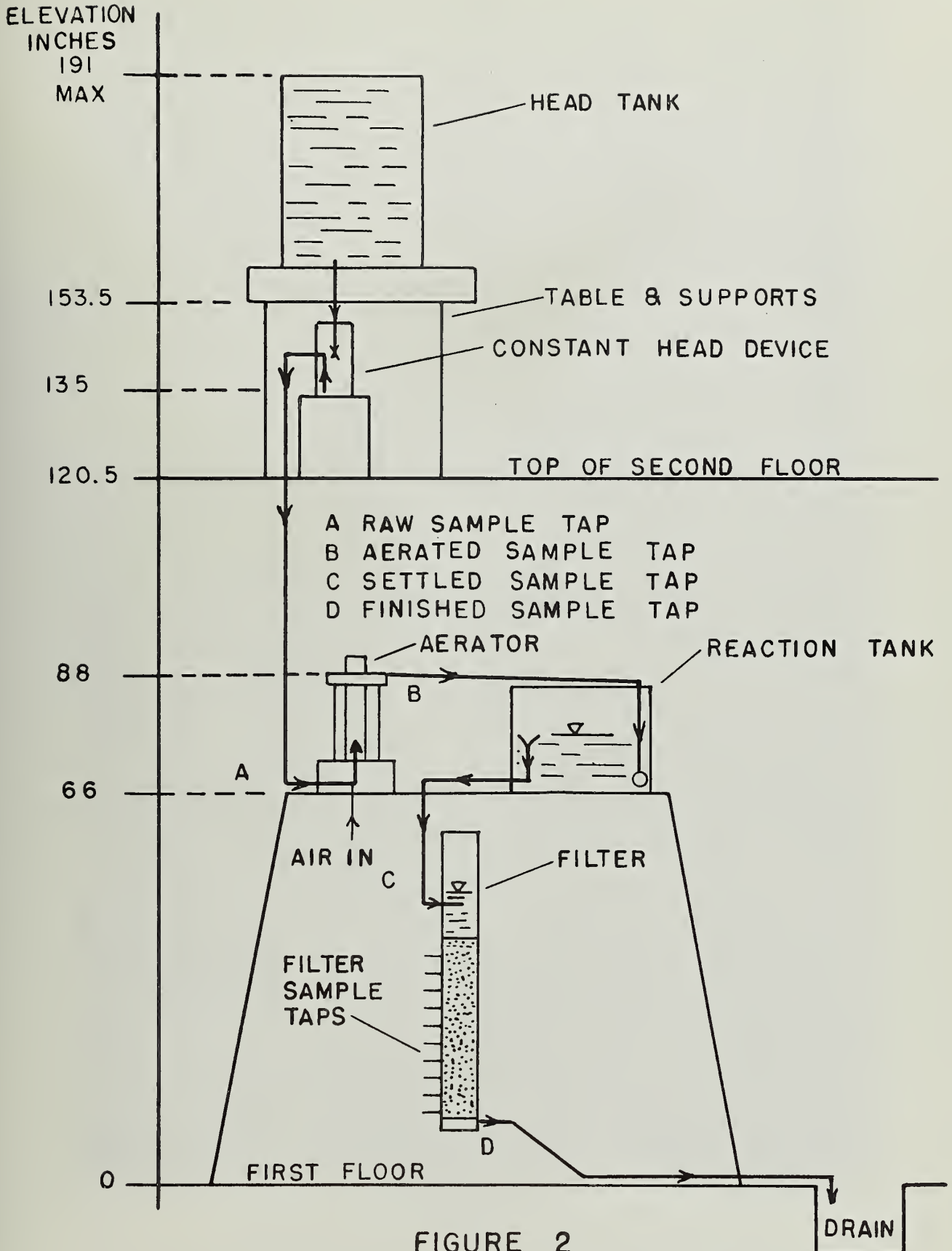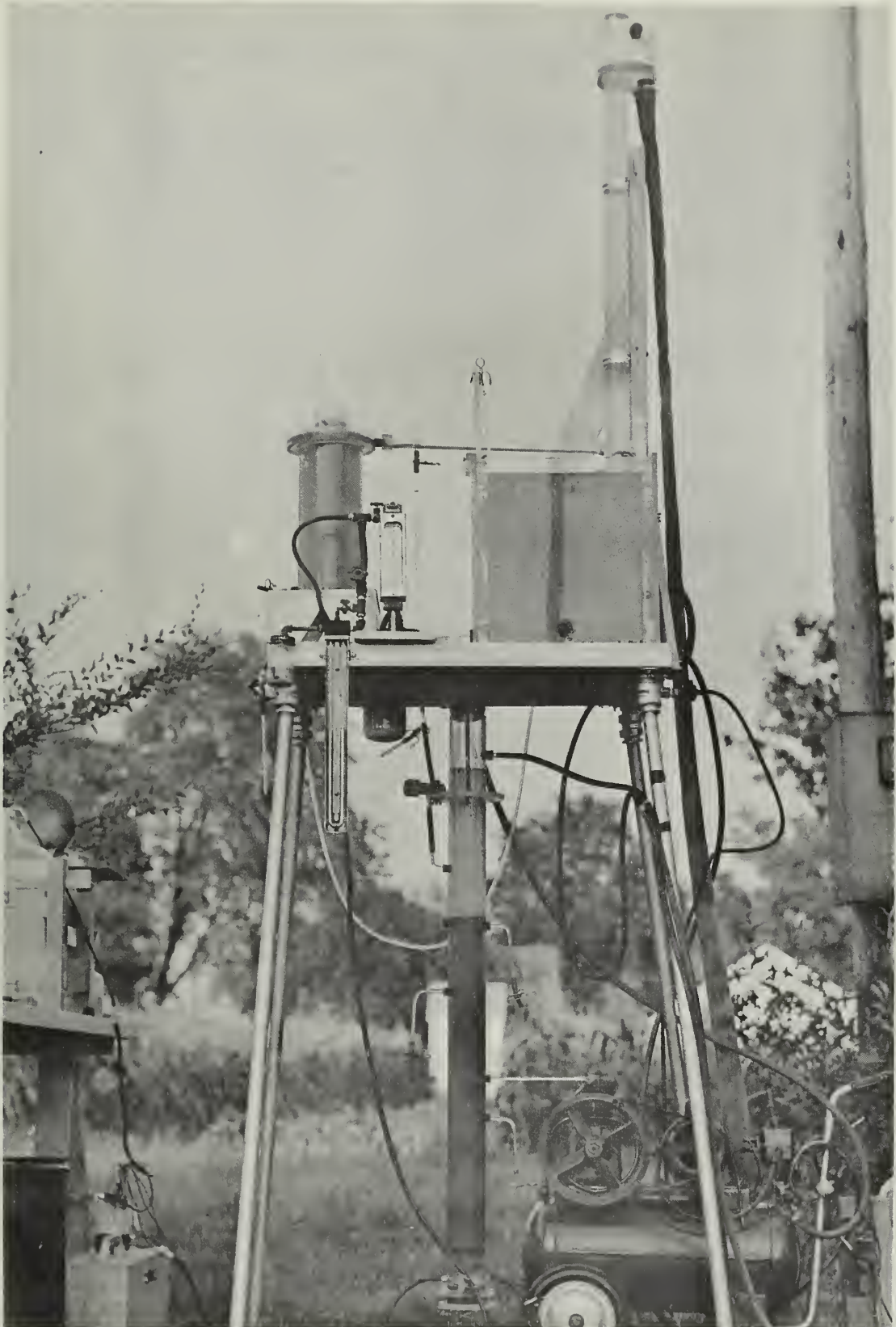
FIGURE 3
The Pilot Plant as Set Up at Cisco, Illinois

The arrangement differs from the laboratory set up only by
the use of the overflow stand pipe in place of the constant head
supply unit.
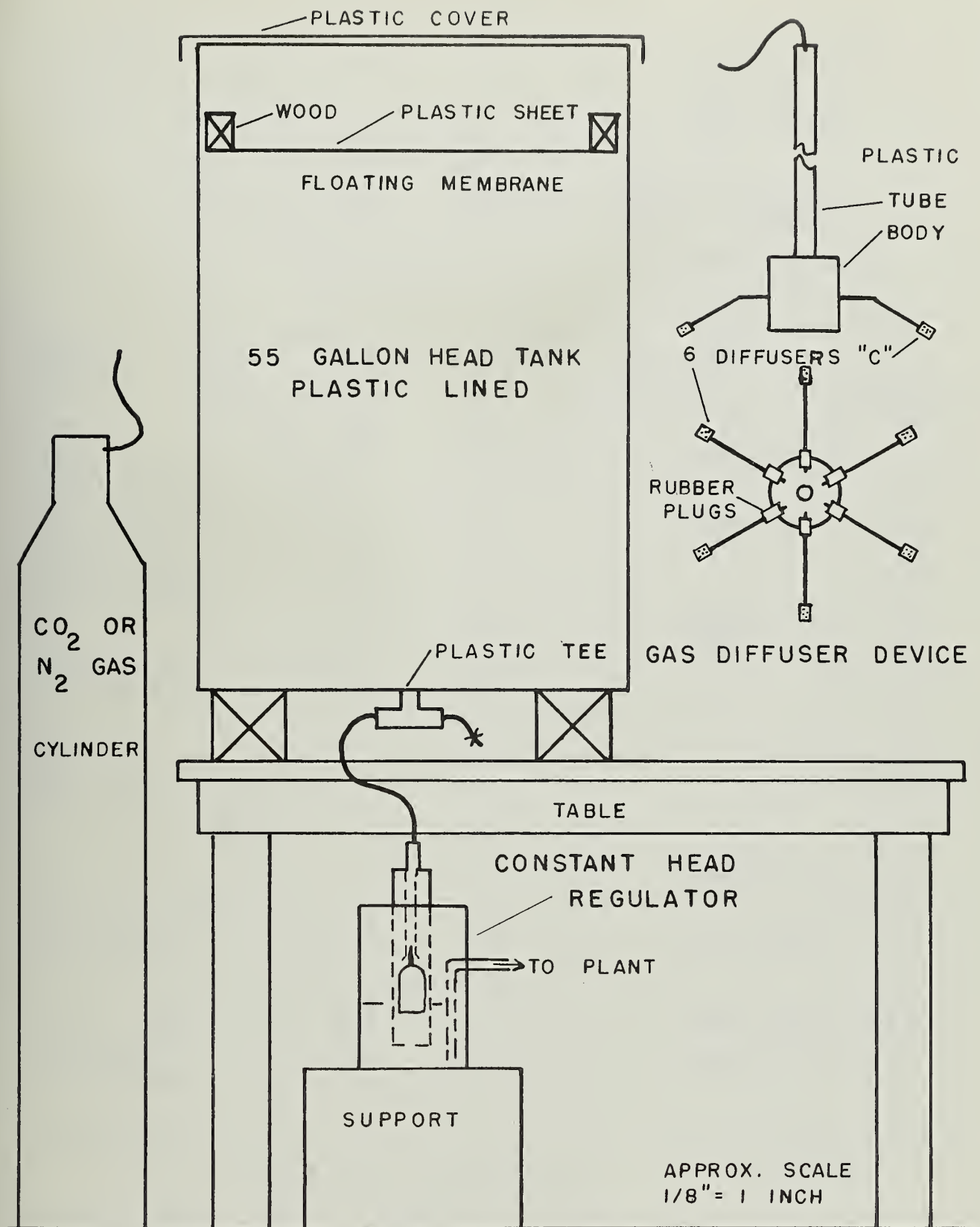
FIGURE 4

FEED TANK & CONSTANT HEAD FLOW REGULATOR

TRIANGULAR SPACER

4 SMALL SPACERS

A

SECTION A-A

ALL PARTS LUCITE UNLESS NOTED

APPROX. SCALE 3/8" = 1 INCH

A

TO TANK

CEMENT OUTLET IN

CEMENT BOTTOM IN

LOOSE FIT

CEMENT SPACERS TO TUBES HERE

CENTRAL TUBE 2" x 1/8" WALL x 16"

BARRIER TUBE 3" x 1/8" WALL x 18"

SHELL TUBE 6" x 1/4" WALL x 16"

DRILL 12 HOLES 1/2" DIA. IN TWO ROWS EQUALLY SPACED AROUND

DRILL 6 HOLES 1" DIA. ONE ROW EQUALLY SPACED AROUND

LOOSE DISC TO LOCATE TUBES

BOTTOM - 1/2" PLASTIC CEMENTED IN

SEE DETAIL

NOZZLE

RUBBER SEAL

DIFFUSER

4 MM GLASS

RUBBER PLUG

GLASS TEE

AIR IN

RUBBER SEAL

WATER IN

DETAIL OF DIFFUSER
2 x SCALE

FIGURE 5
THE AERATOR

houses the inlet nozzle and diffuser. The water spills over the top of the small central tube and passes down the annular space between the central tube and the barrier tube, since the barrier tube extends above the central tube. Holes at the bottom of both tubes permit a division of the flow; thus some water is recirculated up the central tube, and the balance moves into the space between the shell and the barrier tube. Water diverted outward eventually passes over the overflow weir into the collection channel and on to further treatment. Figure 6 shows the aerator in action; the profuse bubble pattern is easily seen, and the air-water "froth" at the top of the central tube can be seen. The walls of the central tube and barrier tube are barely discernable.

The sizing and volume of the aerator were largely a matter of convenience. With a water flow of 416 cc/min (which loads the filter at 2 gallons per minute per square foot) the detention time in the aerator is about 14 minutes; this is quite in agreement with the contact times suggested in the literature for aeration devices.

The compressed air for aeration is supplied at 125 psig either by the central laboratory compressor, or by a portable compressor unit. The air is passed through a trap with glass wool to remove dust, oil, and moisture. A flow regulator is used to keep the flow at a chosen rate. A Rotameter is used to measure the airflow. A needle valve following the Rotameter provides additional control of the air flow rate, and a mercury manometer is connected to measure the pressure after the needle valve. This system provided a sensitive control of the air flow.
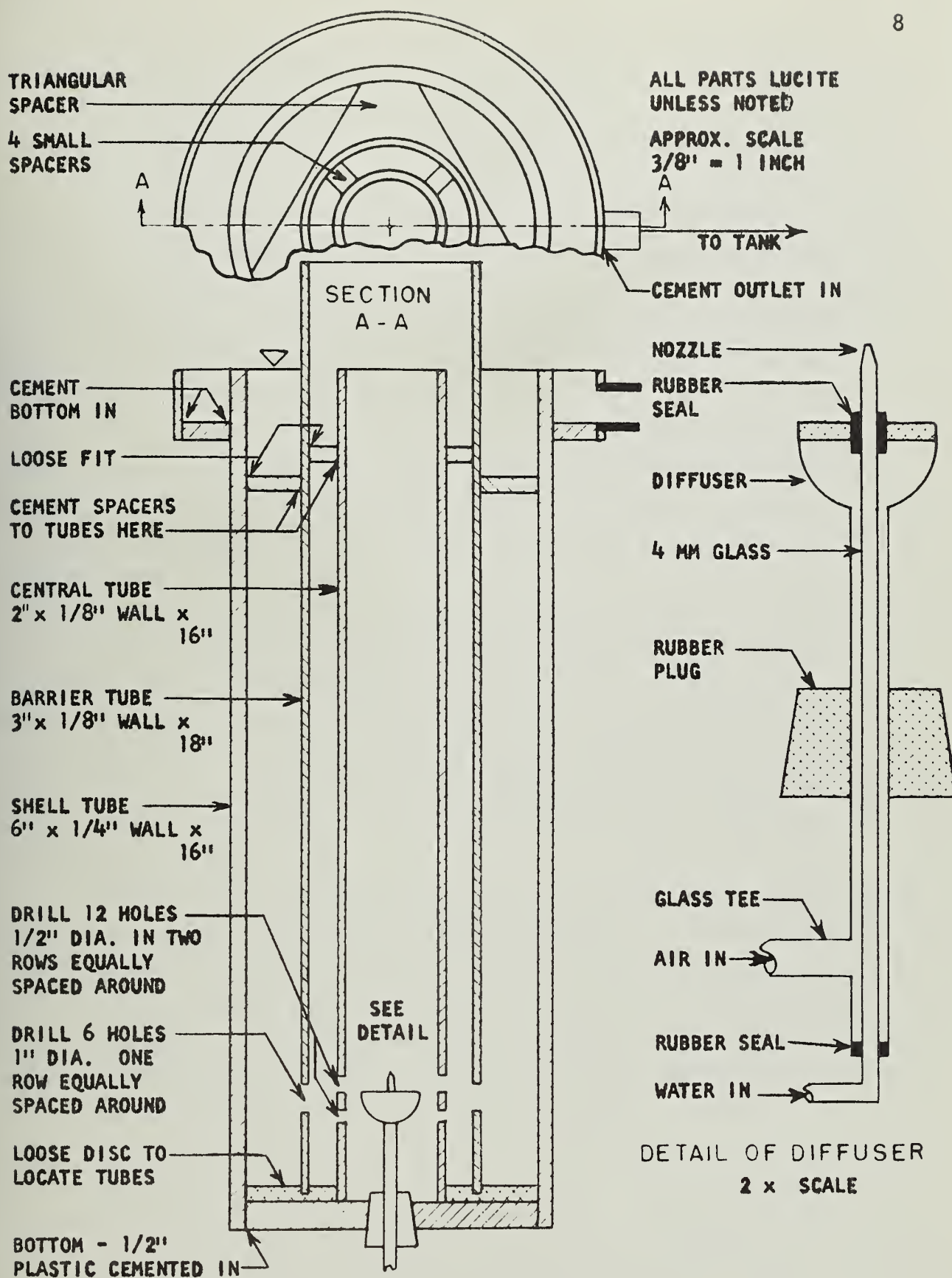
The tank for the combined purpose of providing time for completing the chemical reaction and for sedimentation was designed with a length-to-width ratio of 2 to 1, so that the path any particle traversed from inlet to outlet could be doubled or halved, depending on the orientation of the tank with respect to inlet and outlet connections. The height was made 18 inches so that a 1.5 hour detention at 416 cc/min flow could be studied, since 1.5 to 2 hours represents the maximum usually encountered in practice for the reaction-sedimentation time.

The line connecting the aerator to the reaction tank was constructed so that when chlorine was introduced at the aerator end it would be thoroughly mixed by the time the water entered the reaction tank. This line has a diversion tap for sampling. To facilitate sampling for dissolved oxygen analysis, the diversion tube was constricted to make it flow full without aspirating air. The line between the aerator and reaction tank does not flow full, and the diversion device imposes a turbulence which improves mixing and aeration.

FIGURE 6

The Aerator in Operation

      Attention is directed to the concentric tubes, visible as
faint shadings, and to the holes which permit the division of
the flow.

      The outlet of the collection channel is seen in the upper
right.

Water leaves the reaction tank via the overflow weir and a plastic tube connected to a plastic needle valve immediately ahead of the sand filter inlet. A sampling tap was provided between the weir and the needle valve. The needle valve can be adjusted to maintain the desired water level in the reaction tank. Figure 7 is a diagram of the reaction-sedimentation tank and the inlet-outlet device.

The filter was constructed as a conventional rapid sand filter using a three inch diameter transparent plastic tube. The filter medium has been a carefully screened sharp grain sand. In the laboratory preparation, the random chosen sand was screened into several fractions. The results of the screening were plotted on log-probability paper. Sieve fractions were selected to give a filter sand having an effective grain size of 0.45 mm and a uniformity coefficient of 1.4. A large supply of this sand was prepared, so that the filter could be replenished, as required, with the original mixture. This was done to establish the filter media as nearly constant as possible. The sand bed was held as near as possible at 30 inches, after back-washing. The filter was provided with a backwash connection at the bottom. Backwashing was usually done with laboratory tap water, and was manually controlled to make a bed expansion of about 15 inches (50 per cent). This amount of expansion provided a good scour action, visible through the filter walls. Backwash was continued until the effluent was clear.

The filter column was fitted with a series of sample tubes positioned at various depths and spacing below the sand surface. The sample tubes were 8 mm glass tubes fitted with sintered glass cylinders. Each sintered glass cylinder was centered on the axis of the filter column. The filter column and a detail of the tap locations is shown in Figure 8.

For field studies, an overflow stand pipe with a diversion tee in the bottom was built. The stand pipe is adjustable in height, and maintains a constant head on the supply line, with flows up to 7.0 GPM. Waste water is carried away by a length of fire hose. The diversion tee at the base was faced so that the incoming flow was split; the desired flow for the treatment plant being taken off, and the balance going into the stand pipe, up and over the top weir. It was felt that the water taken off for the treatment plant would be more representative of the true raw water than it would be if it were taken out of the stand pipe itself. Also, possible aeration-oxidation was avoided by this connection. This stand pipe, with the overflow weir and waste water hose is shown in Figure 3.

RUBBER PLUGS

FROM AERATOR

GLASS TEE

SECTION B-B
FULL-SCALE

ADJUSTABLE
BRASS BOLT

TYGON JOINT

LUCITE TANK
8" x 16" x 18" HIGH
INSIDE DIMS.
1/2" WALLS

ALL PARTS
"LUCITE"
UNLESS NOTED

APPROX. SCALE
1/8" = 1 INCH

OUTLET
DEVICE

3" GLASS FUNNEL

1 x 1/8" WALL
TUBE

TYGON TUBE

SECTION A-A

RUBBER PLUG

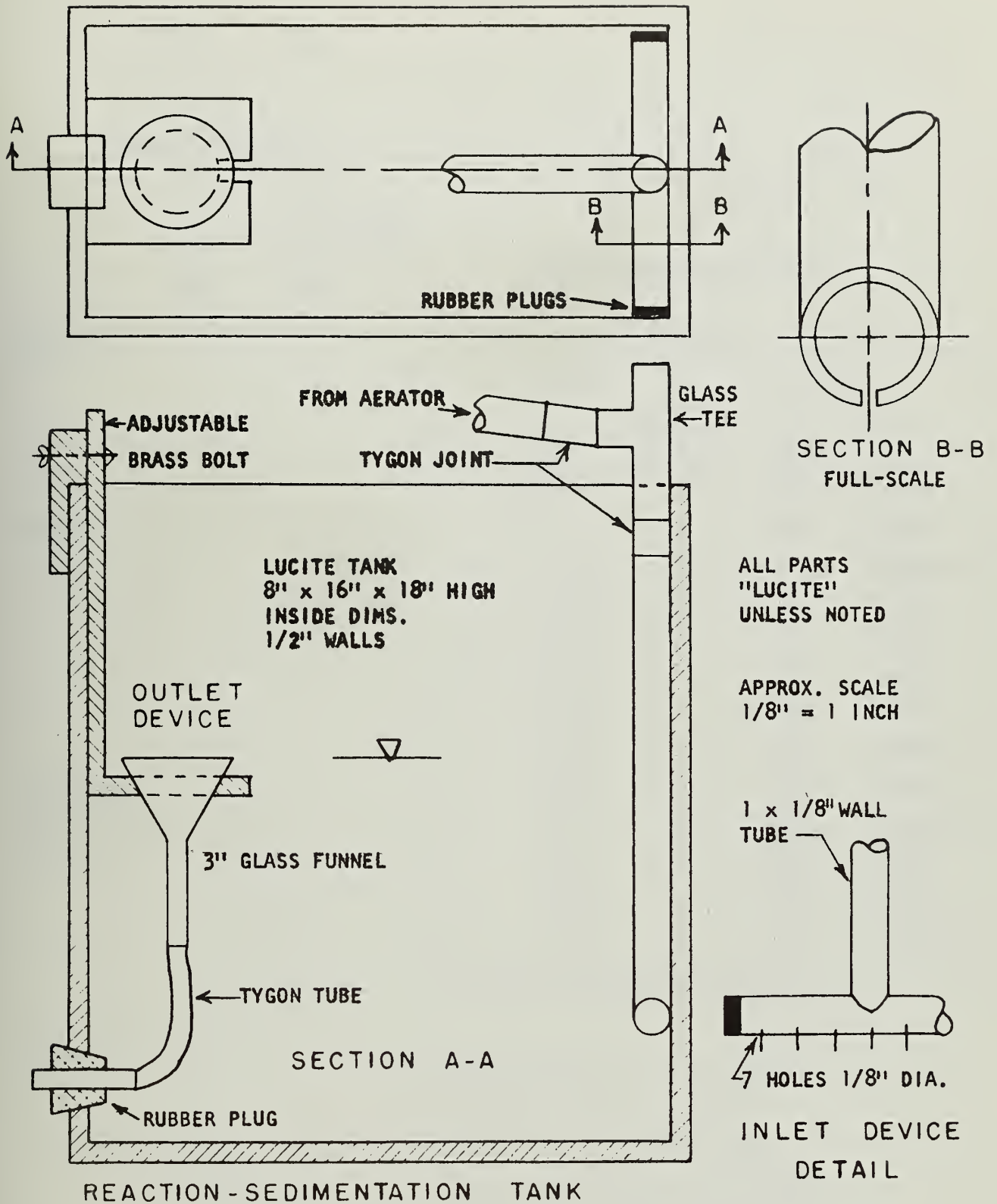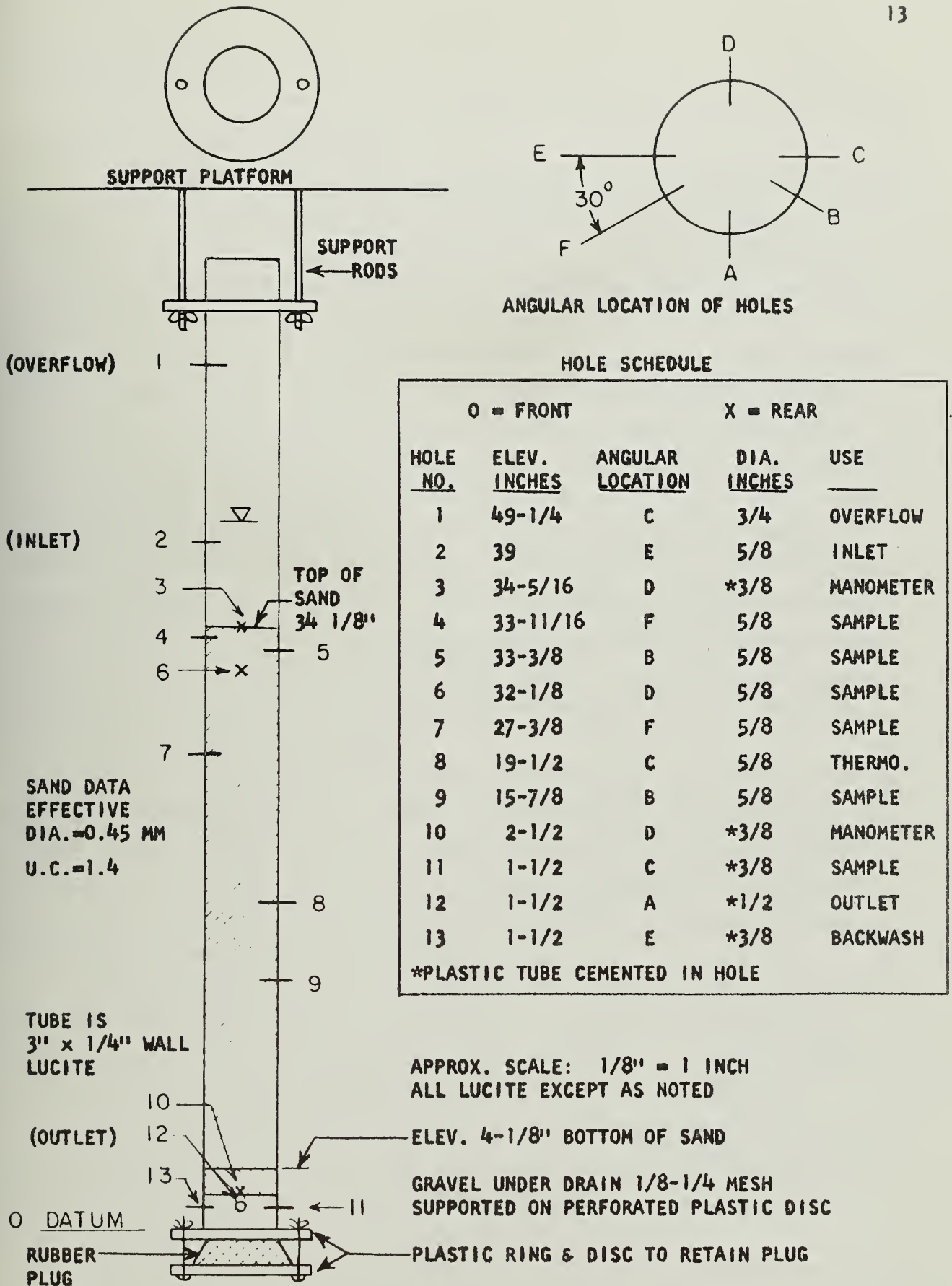7 HOLES 1/8" DIA.

INLET DEVICE
DETAIL

REACTION-SEDIMENTATION TANK

FIGURE 7

REACTION-SEDIMENTATION TANK
INLET AND OUTLET DEVICES

FIGURE 8

SAND FILTER DETAILS

B. Analytical Methods

Table 1 is a summary of the analytical methods used during this study.

C. Water and Equipment Preparation

The synthetic waters were prepared by adding carefully weighed amounts of dry chemical to a measured volume of deoxygenated distilled water--usually 220 liters or 54 gallons, the capacity of the supply tank. Care was taken in filling the tank so as to avoid turbulence and consequent aeration as much as possible.

The solubility of calcium and magnesium carbonate in distilled water is low, so carbon dioxide gas was bubbled through the water to make carbonic acid, which in turn reacted with the carbonate to make soluble bicarbonates. The gas was introduced through six glass diffusers connected to a manifold which was held submerged to the bottom of the tank by the rigid plastic supply pipe. The gas was bubbled in until all the solid chemical was dissolved--usually a period of five to eight hours. The bubbles created some mixing, but occasional mechanical agitation was beneficial. After the carbonate compounds were dissolved, the water was stripped of dissolved oxygen by bubbling compressed high purity dry nitrogen through the same diffuser device. When dissolved oxygen tests showed less than 0.5 mg/l dissolved oxygen present, the iron compound, usually ferrous chloride, was added.

Natural well waters were handled as follows. On the afternoon of the day before a scheduled experiment, 60 gallons of the water to be used were collected in glass carboys. At the time of collection, the collecting equipment was thoroughly flushed until it was felt that representative water was being pumped. The carboys were completely filled with a minimum of turbulence and aeration, and capped with aluminum foil.

The water was analyzed in the field for dissolved oxygen; temperature, pH, and ORP measurements made; and samples for iron analysis were taken and fixed with acid for later determination in the laboratory. Sufficient sample was also collected to make a complete mineral analysis of the raw water.

The filled carboys were transported to the third floor of the laboratory and, on the day of the experiment, carefully syphoned into the feed tank. The surface of the water was protected from aeration by a floating plastic membrane. No gas of any kind was introduced.

For field studies, the equipment was disassembled and transported to a field site. The water was supplied through the overflow stand pipe device; no special handling was required.

Table 1

SUMMARY OF ANALYTICAL METHODS

Determination	SM*	Method Used	Results mg/l as	Comment
Alkalinity	Yes	Electric Titrimeter	$CaCO_3$	
Chloride	Yes	Mohr method	Cl^-	Mercuric nitrate method used for later work.
COD	Yes	Dichromate Reflux	O_2 Consumed	Catalyst generally used
Total Hardness	Yes	EDTA Titration	$CaCO_3$	Commercial indicator used (Univer II)
Calcium Hardness	Yes	EDTA Titration	$CaCO_3$	Commercial indicator used (Calver II)
Total Iron	Yes	Ortho-phenanthroline	Fe	Spectrophotometer; vs. blank of treated, iron free water
Ammonia Nitrogen	Yes	Distillation	N	Distillate collected in H_3BO_4 and titrated with H_2SO_4 on titrimeter
Organic Nitrogen	Yes	Kjeldahl	N	Same as Ammonia Nitrogen
Dissolved Oxygen	Yes	Winkler, modified	O	Azide Modification
pH	Yes	Glass Electrode	pH	Beckman "G" instrument, battery operated Sodium ion neglected
Residue	Yes	Gravimetric	solids	
Sulfate	Yes	Turbidimetric	SO_4	Spectrophotometer and standard curve
Temperature	Yes	Mercury Thermometer	°C	
Acidity	Yes	Electric Titrimeter	$CaCO_3$	Little significance; seldom made
Hydrogen Sulfide	No	Methylene Blue Spectrophotometer	H_2S	Seldom made
Ferrous Iron	No	Ortho-phenanthroline	Fe	Modification of procedure for total iron
Oxidation-Reduction Potential	--	Pt - Calomel	Milli-volts	
Calculated Analysis				
Carbon Dioxide	Yes	Nomograph	CO_2	
Magnesium Hardness	--	Calculation	$CaCO_3$	Difference between total and Calcium Hardness considered as Mg Hardness.

*Standard Methods for the Examination of Water, Sewage and Industrial Wastes, 10th Edition

D. Operation of the Pilot Plant

Each experiment was started by filling, in turn, the aerator, the reaction-sedimentation tank, and the sand filter. Samples for water analysis were taken after about three pore volumes of test water had passed through the sand filter; this insured that the distilled water (kept in the filter between runs) was completely displaced. Air was applied at a rate of about 1600 cc/min during this initial period, as well as during the course of an experiment. After the plant was filled and operating at equilibrium, the hourly sampling to evaluate the operation was started.

The sampling procedure varied with various experiments, but generally the following basic samples were taken:

1. Raw water entering aerator:
   a. Alkalinity
   b. Dissolved oxygen
   c. Iron--always total, and occasionally ferrous
   d. pH
   e. Temperature

2. Aerated water at a point just beyond the aerator collection channel:
   a. Dissolved oxygen
   b. Iron--always total; occasionally ferrous
   c. pH
   d. Temperature, from top of aerator

3. Settled water, at a point between the weir of the reaction tank and the filter inlet regulating valve:
   a. Iron--always total; occasionally ferrous
   b. pH
   c. Temperature, at the weir

4. Filtered water:
   a. Iron--always total, occasionally ferrous
   b. Alkalinity
   c. Dissolved oxygen, occasionally
   d. pH
   e. Temperature

5. Temperature at the mid point of the filter.

As soon as possible after an experiment, the equipment was washed up with hydrochloric acid (except the sand filter) to remove iron and $CaCO_3$ deposits. The filter was backwashed vigorously, then left filled with distilled water.

III EXPERIMENTAL RESULTS

A. Preparation of Synthetic Ground Water

Nine experimental synthetic ground waters were successfully prepared and used with the experimental pilot plant in the laboratory. Various combinations of nitrogen stripping, carbonation, and chemical additions were tried in order to find the most economical combination (in terms of gas consumption) and the most "satisfactory" iron bearing water in terms of stability of the ferrous iron. This stability was evaluated by the length of time between the addition of a ferrous compound and the observation of a yellow or red-brown color typical of ferric iron in the water.

The choice of chemicals to provide hardness and alkalinity in desired ratios was based on the selection of the most soluble compound available, which would not introduce an undesired anion. The iron compound was selected to provide ferrous ions and a desirable anion; usually ferrous chloride was used. Table 2 is a summary of the procedure and sequence of stripping, carbonating, chemical addition, final character, and the observed time until the ferric ion was visually noted.

Since natural well waters are more or less stable in their ferrous-ferric ratio; e.g., the yellow color is either present immediately and remains quite uniform, or it does not appear for quite some time, the evaluation of the synthetic waters was made in terms of time of appearance of yellow color.

The sequence and duration of applying the CO_2 gas was determined by the need for carbonation to convert insoluble carbonates to soluble bicarbonates. The N_2 was used for stripping dissolved oxygen and for mixing chemicals, and was applied as needed for these purposes. As Table 2 shows, CO_2 also turned out to be effective as a stripping gas, so N_2 stripping prior to adding carbonates and sulfates was discontinued. Table 2 also indicates that waters with a hardness approximately equal to, or greater than, the alkalinity maintain a ferrous stability longer than those with excess alkalinity.

The dissolved oxygen at the time of addition of the ferrous compound was obviously important, since as little as 0.5 mg/l DO could oxidize all of the 3 mg/l of ferrous iron added. So as to prevent the immediate oxidation of ferrous iron, it was found that the DO concentration should not exceed 0.10 to 0.15 mg/l following stripping with either N_2 or CO_2. However, there are other compounds which apparently can also influence this oxidation rate. The presence of free CO_2 in the water when the iron compound was added seemed to show a direct

Table 2

SUMMARY OF SYNTHETIC GROUND WATER COMPOSITION

	1	2		3	4	5		6	7	8	
	Water	N_2		CO_2	Chem.	CO_2		Chem.	CO_2	N_2	
No.	Type	Hrs.	End DO	Hrs.	Added	Hrs.	End DO	Added	Hrs.	Hrs.	End DO
2	F	4	1.85	No	CaCO$_3$ MgSO$_4$	12	1.5	No	No	NO	
3	F	5	0.5	No	CaCO$_3$ MgSO$_4$	12	0.22	No	No	1	0.15
4	C	7	0.27	No	CaCO$_3$ MgCO$_3$	11	0.75	No	No	No	
5	C	No		No	CaCO$_3$ MgCO$_3$	7	0.55	No	No	No	
6	D	No		No	CaCO$_3$ MgCO$_3$	12		No	No	2	0.12
7	B	No		No	CaCO$_3$ MgCO$_3$	12		No	No	2	0.12
8	A	No		4	CaCO$_3$ MgSO$_4$	7		NaHCO$_3$	2	9	0.05
9	B	No		No	CaCO$_3$ MgCO$_3$	15		CaCO$_3$ NaHCO$_3$ MgSO$_4$	No	10	0.15
10	G	No		No	CaCO$_3$	19		NaHCO$_3$ MgSO$_4$	4	1	0.08

Table 2, Continued

No.	Water Type	Chem. Added	N₂ Hrs.	End DO	Iron Added as	N₂ Hrs.	CO₂ Hrs.	Alkalinity mg/l	Hardness mg/l	pH	CO₂ Calc, mg/l	Time for Yellow hrs.
2	F	No			$FeSO_4$	No	During exp.	125	285	5.8	280	5
3	F	No			$FeSO_4$	During exp.	No	110	250	6.4	85	4
4	C	No			$FeCl_2$	During exp.	No	245	260	7.2	28	6
5	C	No			$FeCl_2$	No	During exp.	245	250	6.8	75	11
6	D	No			$FeCl_2$	During exp.	Blanket*	390	300	6.7	110	3
7	B	NH_4Cl_2 Na_2SO_4	2	0.10	$FeCl_2$	During exp.	Blanket	393	300	6.9	65	2 1/2
8	A	No	No		$FeCl_2$	During exp.	Blanket	396	290	7.5	34	1
9	B	Na_2SO_3	1	0	$FeCl_2$	During exp.	Blanket	405	305	6.8	85	1
10	G	Na_2SO_3	1/2	0	$FeCl_2$	During exp.	Blanket	410	295	6.8	45	2

* "Blanket" denotes gas maintained over water surface during run.

All gas was introduced by bubble diffusion.

correlation with the stability of the ferrous iron. It appeared that at least 30 mg/l free CO_2 was necessary for a one hour stability, while 100 mg/l or more CO_2 extended the stability to several hours.

The pH of the water was observed to be probably the most precise indicator of stability. The experimental waters showed a linear correlation between pH and stability, Figure 9. Waters for which the pH at the time of iron addition was not accurately known have been eliminated. Data to extend the curve of Figure 9 below pH 5.8 are not available; however, it is expected that the stability would become asymptotic to the time axis at some lower pH. Ferrous iron standard solutions, at low pH, keep indefinitely.

The observed pH-stability is in agreement with the CO_2-stability observations; the high CO_2 concentrations create the lower pH values, and these lower pH waters were found to be the most stable with respect to ferrous iron.

The entire study of synthetic waters was based on a system containing no organic matter and, thus, no organic complex of the iron forms. This is not truly representative of the surface waters which might be encountered, but it is reasonable for many ground waters. As has been pointed out before, the organic complexes hold the iron in solution for an indefinite time, and are quite independent of pH and CO_2 conditions.

B. Characterization of the Waters Tested

The 9 synthetic water and 14 natural water experiments performed embrace nine "characteristic" waters or groups of waters with very similar mineral constituents. Although the experiments were performed on the 9 synthetic waters first, followed by 8 laboratory and 6 field studies of natural waters, it seems more desirable to discuss the results of the experiments arranged according to mineral characteristics.

The following outline is used in correlating waters in terms of mineral characteristics.

Water Characteristics		Water Designation
I Nitrogen and Sulfate Variable: Iron 3-6 mg/l		
A. High Sulfate 50-75 mg/l		
1. Nitrogen 0 mg/l		A
2. Nitrogen 4-6 mg/l		B
B. Low Sulfate 0-2 mg/l		
1. Nitrogen 0 mg/l		C
2. Nitrogen 4-6 mg/l		D
3. Nitrogen 14-16 mg/l		E

II   Non-carbonate Hardness Present: Iron 3-6 mg/l   F

III   Reducing Agent Present, Sulfite added: Iron 3-6 mg/l; G
      Nitrogen, 0 mg/l; Sulfate, 50-75 mg/l; chloride,
                                             0-15 mg/l.

IV   Chloride High: Iron 3-6 mg/l; Nitrogen, 0 mg/l;   H
      Sulfate, 0-2 mg/l; Chloride, 50-60 mg/l.

V   Iron High: Iron, 12-17 mg/l; Nitrogen, 14-16 mg/l;   J
      Sulfate 0-2 mg/l; Chloride, 0-15 mg/l.

Hardness and alkalinity varied, but the variation is not significant in the results.

The various waters, their source, and their characteristics are summarized in Table 3. The letter and subscript nomenclature will be kept uniform throughout the presentation of results and the discussions which follow.

C. The Aeration Unit and Dissolved Oxygen Study

The primary function of the multiple pass aerator was to subject the water to vigorous aeration; secondarily, to remove any particles (of floc, etc.) large enough to settle against the upflow velocity.

The measured volume of the aerator was 5.9 liters. At a flow rate of 416 cc/min, this provided a theoretical detention time of 14.2 minutes. From a study of the detention time by the salt tracer technique, it was found that the flow-through was almost ideal.

The action of the aerator as an upflow clarifier might be expected to remove some iron if flocs large enough to settle out were formed. This floc formation would depend upon the rate of the oxidation reaction and the coagulation phenomenon. As subsequent discussion will show, the aerator appeared responsible for some iron removal.

During each experiment, a complete record of dissolved oxygen of the water before and after aeration was made. Air flow was maintained constant and the same for all experiments, so as to eliminate one variable throughout the entire study. Excluding the waters with a high sulfate concentration, the aerator produced a water with a final mean DO of 6.9 ± 1.0 mg/l. In general, this represented a DO increase of 6.36 ± 0.8 mg/l. In terms of per cent of saturation, the uniformity of the performance on all types of water was even more noticeable. The final mean DO was 79.5 per cent of saturation, and represents a mean increase of 74.0 per cent of saturation. This performance included water with temperatures from 13° C to 27° C. Table 4 summarizes the performance of the

Synthetic Water

○ FeSO$_4$ Used

⊕ FeCl$_2$ Used

Hours to Appearance of Yellow Color in Supply
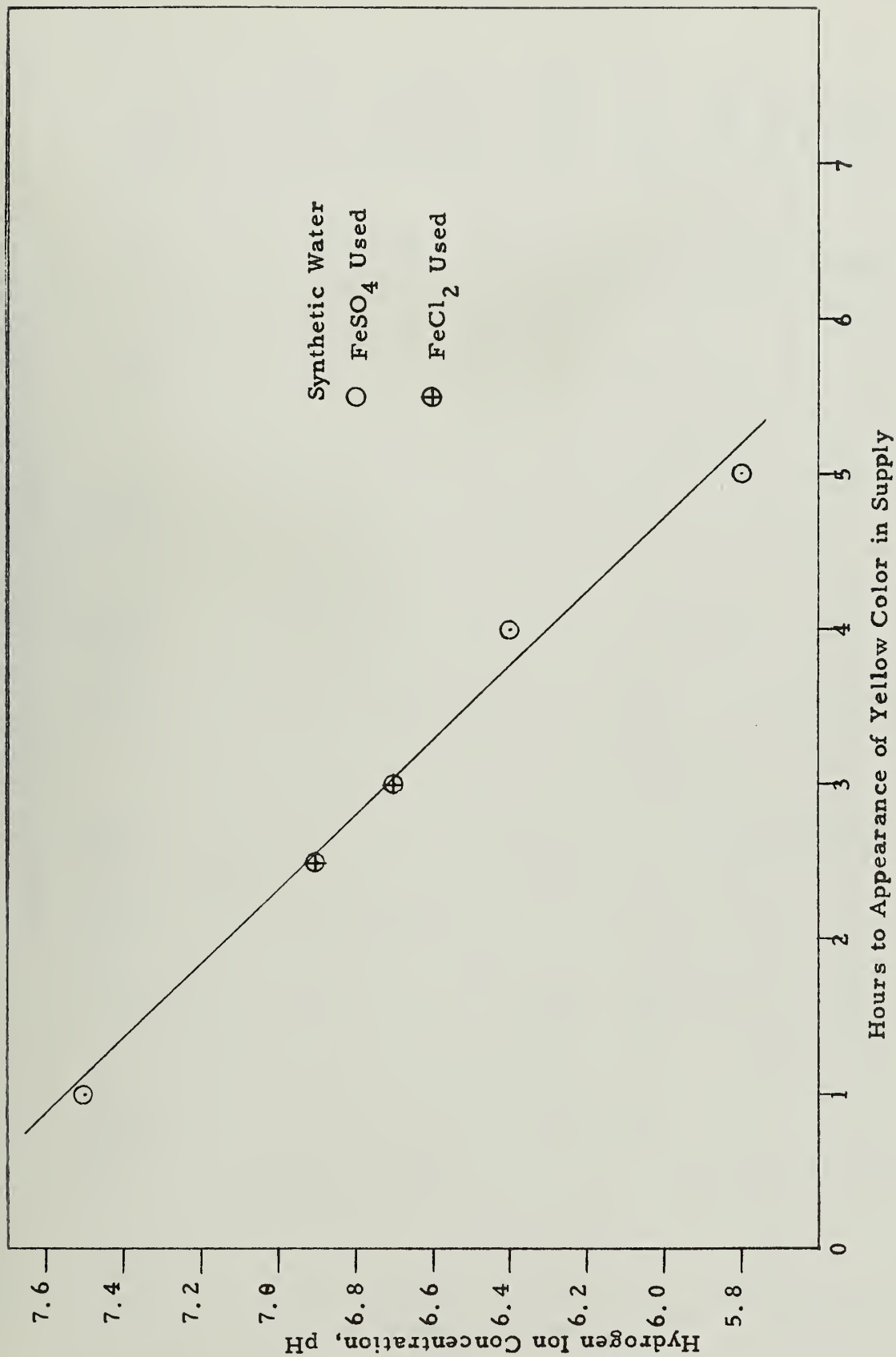
FIGURE 9

pH and Time Before Ferric Oxide is Evident As A Color
Change in the Supply

Hydrogen Ion Concentration, pH

Table 3

GROUPING OF WATERS BY MINERAL CHARACTER

Group Letter	Sulfate 0 mg/l	Sulfate 50-75 mg/l	Total Nitrogen 0-2 mg/l	Total Nitrogen 4-6 mg/l	Total Nitrogen 14-16 mg/l	Chloride 0-15 mg/l	Chloride 50-60 mg/l	Non-Carb. Hard	Red. Agent	Exp. No.	Source
A		X	X			X				8	Synthetic
B		X		X		X				7	Synthetic
C 1	X		X			X				4	Synthetic
C 2	X		X			X				5	Synthetic
D 1	X			X		X				6	Synthetic
D 2	X			X		X				13	Natural
D 3	X			X		X				14	Natural
D 4	X			X		X				16	Natural
E	X	X			X	X				12	Natural
F 1		X	X			X		X		2	Synthetic
F 2		X	X			X		X		3	Synthetic
G 1	X	X	X			X			X	9	Synthetic
G 2	X	X	X			X			X	10	Synthetic
H 1	X		X				X			11	Natural
H 2	X		X				X			15	Natural
J 1	X				X	X				17	Natural
J 2	X				X	X				18	Natural
J 3	X				X	X				19	Field
J 4	X				X	X				20	Field
J 5	X				X	X				21	Field
J 6	X				X	X				22	Field
J 7	X				X	X				23	Field
J 8	X				X	X				24	Field

Table 4

SUMMARY OF AERATOR PERFORMANCE

Experiment No.	DO After Aeration mg/l	Percent Saturation After Aeration	Gain in DO mg/l	Increase of Percent Saturation
Synthetic, in Laboratory				
3	6.41	79.0	6.02	74.2
4	7.33	87.2	6.60	78.6
5	7.03	85.6	6.93	84.4
6	6.65	83.9	6.53	82.4
7	7.36	88.0	6.07	71.4
8	7.15	85.4	6.38	76.1
9	6.85	85.3	6.81	84.8
10	4.81	67.3	4.81	67.5
Mean	6.7	82.7	6.3	77.4
Natural, in Laboratory				
11	7.39	84.6	6.57	75.1
12	6.87	82.0	6.51	77.6
13	7.40	84.4	6.59	77.5
14	6.77	86.1	5.54	72.1
15	7.36	84.2	6.19	70.8
16	7.33	84.5	6.05	67.7
17	6.39	77.5	6.39	77.5
18	6.66	80.4	6.25	77.4
Mean	7.1	83.0	6.3	74.5
Natural, in Field				
19	6.87	71.1	6.87	71.1
20	7.07	70.4	7.07	70.4
21	7.83	77.3	6.36	71.9
22	6.10	60.4	6.10	60.4
23	6.88	65.7	6.88	65.7
24	6.12	60.5	6.12	60.5
Mean	6.8	67.6	6.5	66.7

aerator; the grouping into synthetic water experiments, laboratory natural water experiments, and field natural water experiments shows small but significant differences in performance.

The study of dissolved oxygen concentrations associated with treatment unit processes following aeration was confined to the J series natural water which contained large iron concentrations and was the most difficult to treat for complete iron removal. Table 5 summarizes the concentrations of DO found after aeration, after reaction-sedimentation, and after filtration. The theoretical consumption of oxygen for oxidation of ferrous iron is 0.14 mg. for every 1.0 mg. of iron removed but the average DO decrease observed was only 0.07 mg. which implies that 50 per cent of the total iron removed by the reaction-sedimentation plus filtration had not been oxidized by the time the water left the aerator, but was oxidized (and later removed) by the reaction-sedimentation unit followed by filtration.

D. Iron Removal

The basic objective of the entire experimental work was to remove iron from waters with varying characteristics.

The method of aeration, reaction-sedimentation and filtration successfully removed the iron from all experimental waters except one, and, in subsequent experiments, this water was successfully treated. Table 6 shows the overall per cent iron removed during each experiment. The waters used are grouped according to the scheme presented earlier in this section. Table 7 is a statistical summary of the total iron analysis data accumulated. Mean, mode, maximum and minimum values for concentrations of iron at each sampling point of each experiment are shown. By examination, it is evident that the mean values are representative of the concentrations of each sampling point, despite an occasional wide divergence.

Table 8 is a tabulation showing the iron removal effected by the aeration process alone. The aerator removed iron by sedimentation of floc as previously discussed, and by the formation of insoluble oxide films which adhered to the interior surfaces of the aerator. The variation in iron removal was great among the groups; the conclusion drawn is that iron removal during aeration was greatest and most consistant for the natural waters brought to the laboratory for study. The variation among waters in the same group indicated that the iron removal during aeration was influenced by some characteristic other than those evaluated in these early studies.

Table 5

OXYGEN CHANGES DURING IRON REMOVAL BY SEDIMENTATION
& FILTRATION FIELD STUDIES, CISCO, ILLINOIS

Parameter Measured or Calculated	Experiment Number					
	19	20	21	22	23	24
DO after aeration mg/l	6.78	7.07	7.83	6.10	6.88	6.40
DO after sedimentation, mg/l	---	---	7.85	6.31	Not used	6.45
Change, sedimentation	+0.10*	+0.10*	+0.02	+0.21	---	+0.05
Iron removed by sedimentation, mg/l	0.0	0.04	0.0	0.0	---	0.0
DO after sedimentation, mg/l	6.88*	7.17*	7.85	6.31	Not used	6.45
DO after filter mg/l	5.96	6.46	6.36	5.45	5.97	6.34
Change, filtration	0.92	0.61	1.49	0.86	---	0.11
Iron removed by filtration, mg/l	10.68	10.40	11.32	10.90	11.05	11.09
Ratio Fe/ DO	13.0	17.1	7.6	12.6	12.1	10.08
Total DO change from after aeration to effluent mg/l	-0.82	-0.61	-1.47	-0.65	-0.91	-0.06
Total iron change for above mg/l	10.47	10.44	10.80	10.56	11.05	10.80
Ratio DO/ iron	0.08	0.06	0.13	0.06	0.08	0.01

Expected DO change: 0.14 mg/l for 1 mg/l iron change

Found DO change 0.07, or 50 per cent

*Best estimate from limited data No. 21 & 22.

Table 6

REMOVAL OF IRON BY AERATION PLUS
REACTION-SEDIMENTATION PLUS FILTRATION

Water		Per Cent of
Group	Type	Applied Iron Removed
A	Synthetic	100.0
B	Synthetic	99.5
C 1	Synthetic	99.8
C 2	Synthetic	99.0
D 1	Synthetic	100.0
D 2	Natural	99.5
D 3	Natural	99.5
D 4	Natural	100.0
E	Natural	99.0
F 1	Synthetic	99.0
F 2	Synthetic	99.6
G 1	Synthetic	100.0
G 2	Synthetic	100.0
H 1	Natural	99.5
H 2	Natural	97.7
J 1	Natural	28.9
J 2	Natural	99.7
J 3	Natural - Field	98.5
J 4	Natural - Field	97.5
J 5	Natural - Field	97.8
J 6	Natural - Field	97.7
J 7	Natural - Field	97.9
J 8	Natural - Field	99.7

Average including J 1   96.2 per cent

Average without J 1   99.5 per cent

Table 7

STATISTICAL TREATMENT OF IRON ANALYSIS DATA

Water	Exp. No.	Group Type	No. Samples	Raw Water Iron Present mg/l				Aerated Water Iron Present mg/l				Settled Water Iron Present mg/l				Finished Water Iron Present mg/l			
				Mean	Mode	Min.	Max.	Mean	Mode	Min.	Max.	Mean	Mode	Min.	Max.	Mean	Mode	Min.	Max.
Synthetic	8	A	8	5.10	5.8	3.0	5.8	2.87	2.9	2.7	3.2	2.51	2.5	2.4	2.8	0.00	0.00	0.00	0.00
Synthetic	7	B	8	3.26	3.3	3.0	3.6	2.86	2.8	2.7	3.3	2.60	2.5	2.5	2.7	0.02	0.02	0.00	0.04
Synthetic	4	C 1	8	4.45	4.5	3.1	5.1	2.89	2.8	2.7	3.4	2.91	2.9	2.7	3.3	0.01	0.00	0.00	0.03
Synthetic	5	C 2	8	3.13	3.1	3.1	3.2	3.03	2.8	2.6	3.6	2.77	2.7	2.7	2.9	0.03	0.00	0.00	0.20
Synthetic	6	D 1	8	3.21	3.1	3.0	3.6	2.95	2.9	2.8	3.3	2.73	2.8	2.7	3.0	0.00	0.00	0.00	0.00
Natural	13	D 2	9	4.53	4.5	3.8	5.0	3.60	3.6	3.2	3.7	3.66	3.6	3.4	3.8	0.02	0.01	0.00	0.06
Natural	14	D 3	8	4.48	4.7	3.3	5.8	3.07	3.1	2.6	3.2	3.12	3.1	2.8	3.3	0.01	0.00	0.00	0.04
Natural	16	D 4	9	3.92	4.1	3.1	4.3	---	---	---	---	3.06	3.1	2.6	3.2	0.00	0.00	0.00	0.00
Natural	12	E	8	5.06	None	4.1	5.7	3.84	3.9	3.7	4.0	3.88	3.8	3.6	4.1	0.04	0.04	0.02	0.07
Synthetic	2	F 1	8	2.32	2.3	2.3	2.5	2.19	2.2	2.0	2.3	2.78	2.5	2.1	3.6	0.02	0.01	0.01	0.05
Synthetic	3	F 2	7	2.89	2.9	2.8	3.0	2.84	2.8	2.7	2.9	2.82	2.8	2.6	3.0	0.01	0.00	0.00	0.04
Synthetic	9	G 1	8	3.18	2.9	2.9	4.0	2.84	2.6	2.6	3.3	2.70	2.7	2.6	2.9	0.00	0.00	0.00	0.00
Synthetic	10	G 2	8	5.26	None	4.1	8.9	2.89	2.9	2.7	3.2	2.75	2.7	2.6	3.1	0.00	0.00	0.00	0.02
Natural	11	H 1	8	2.31	2.3	2.1	3.1	1.79	1.8	1.7	1.9	1.82	1.8	1.8	1.9	0.01	0.00	0.00	0.04
Natural	15	H 2	9	2.77	2.8	2.1	3.9	1.79	1.8	1.7	1.9	1.81	1.8	1.7	2.0	0.08	0.04	0.00	0.44
Natural	17	J 1	9	17.92	16.7	14.3	22.5	12.77	13.0	10.8	13.4	12.51	12.6	11.1	13.1	12.74	None	0.17	23.70
Natural	18	J 2	9	16.38	16.0	9.6	21.8	11.40	11.0	9.2	13.1	10.99	11.2	10.3	11.5	0.03	0.01	0.00	0.03
Field	19	J 3	11	11.24	11.0	11.0	11.5	10.55	10.5	10.3	10.8	10.76	11.0	10.3	11.0	0.08	0.04	0.20	0.38
Field	20	J 4	10	11.39	11.3	11.3	11.6	10.72	10.7	10.0	11.2	10.68	10.6	10.0	11.3	0.28	0.00	0.00	1.10
Field	21	J 5	10	11.70	11.7	11.6	11.7	11.05	11.4	7.2	11.8	11.58	11.4	10.4	12.6	0.25	None	0.10	1.00
Field	22	J 6	9	11.15	---	---	---	10.81	11.1	9.8	11.3	11.15	11.1	10.7	11.6	0.25	---	---	---
Field	23	J 7	10	11.29	None	11.0	11.7	---	---	---	---	11.28	None	10.9	11.7	0.23	0.10	0.02	7.00
Field	24	J 8	10	11.36	None	11.0	11.9	10.84	11.0	10.9	11.5	11.13	11.0	10.6	11.8	0.04	0.00	0.00	0.14

Table 8

REMOVAL OF IRON BY THE AERATOR

Water		Per Cent of
Group	Type	Applied Iron Removed
A	Synthetic	44
B	Synthetic	12
C 1	Synthetic	35 Avg. 19
C 2	Synthetic	3.2
D 1	Synthetic	8.1
D 2	Natural	20.5 Avg. 20
D 3	Natural	31.4
D 4	Natural	Incomplete
E	Natural	24
F 1	Synthetic	5.6 Avg. 3.6
F 2	Synthetic	1.7
G 1	Synthetic	10.7 Avg. 27.8
G 2	Synthetic	45
H 1	Natural	22.5 Avg. 29
H 2	Natural	35.4
J 1	Natural	28.7
J 2	Natural	30.4 Avg. 29.6
J 3	Natural - Field	6.1
J 4	Natural - Field	5.9
J 5	Natural - Field	5.6
J 6	Natural - Field	3.0 Avg. 4.3
J 7	Natural - Field	0.1
J 8	Natural - Field	5.0

Table 9 is a tabulation showing the removal of iron by the reaction-sedimentation process. The results of removal of iron by the reaction-sedimentation process were more consistant than those for aeration, and showed that zero to about 12 per cent removal can be accomplished by sedimentation after aeration. The synthetic waters showed the most reduction of iron by sedimentation, while the natural waters in the laboratory studies and field studies showed very little removal.

Table 10 summarizes the removal of iron based on that amount of iron applied to the sand filter. With the exception of J 1, the sand filter averages 98.9 per cent removal of the iron applied. The lower per cent removals are for natural waters, and occur with both field studies and laboratory studies.

Table 11 gives the percentage of the total iron in the raw water removed by the sand filter, when the removal is accomplished by aeration, reaction plus sedimentation, and sand filtration. It is readily seen that the removal varies from 50 to 98 per cent, and shows two trends with respect to various waters. First, there are situations where the removal of the iron is almost entirely accomplished by the sand filter. Experiments F 1 and 2 (waters with the hardness and alkalinity approximately equal) demonstrated this. The waters used in the field studies also showed that most of the iron removal occurred during the sand filtration. The second trend is that some waters, notably those with high sulfate concentrations, settled more successfully than the others. Waters with alkalinity greater than hardness oxidized very easily, but removal by the filter appeared unaffected.

E. Carbon Dioxide Reduction and pH Considerations

The carbon dioxide (CO_2) study was confined to an evaluation of the CO_2 reduction and accompanying pH changes resulting from aeration, and to the relationship between the changes, the water group characteristics, and iron removal. The mean value of CO_2 removed was 77 per cent, the maximum was 88 per cent, and the minimum 56 per cent. The change in pH is an important and quite obvious result of changing the CO_2 content of the water. There was a significant increase in pH of the water following aeration. The reaction-sedimentation process and the sand filtration generally increased the pH slightly, but occasionally a water showed a drop in pH. The final pH of the waters investigated was above 7.4 in all but one experiment. There was no relationship between final pH achieved and the degree of iron removal.

Table 9

REMOVAL OF IRON BY THE REACTION-SEDIMENTATION TANK

Water		Per Cent of
Group	Type	Applied Iron Removed
A	Synthetic	12.5
B	Synthetic	9.1
C 1	Synthetic	0.0
C 2	Synthetic	8.6
D 1	Synthetic	7.5
D 2	Natural	0.0
D 3	Natural	0.0
D 4	Natural	Incomplete data
E	Natural	0.0
F 1	Synthetic	Incomplete data
F 2	Synthetic	0.7
G 1	Synthetic	4.9
G 2	Synthetic	4.7
H 1	Natural	0.0
H 2	Natural	0.0
J 1	Natural	2.2
J 2	Natural	3.6
J 3	Natural - Field	0.0
J 4	Natural - Field	0.4
J 5	Natural - Field	0.0
J 6	Natural - Field	0.0
J 7	Natural - Field	---
J 8	Natural - Field	0.0

Table 10

REMOVAL OF IRON BY THE SAND FILTER AS A
UNIT PROCESS

Water		Per Cent of
Group	Type	Applied Iron Removed
A	Synthetic	100.0
B	Synthetic	99.0
C 1	Synthetic	99.0
C 2	Synthetic	99.0
D 1	Synthetic	100.0
D 2	Natural	99.5
D 3	Natural	99.7
D 4	Natural	100.0
E	Natural	99.0
F 1	Synthetic	99.0
F 2	Synthetic	99.5
G 1	Synthetic	100.0
G 2	Synthetic	100.0
H 1	Natural	99.4
H 2	Natural	95.5
J 1	Natural	0.0
J 2	Natural	99.8
J 3	Natural - Field	99.0
J 4	Natural - Field	97.3
J 5	Natural - Field	98.0
J 6	Natural - Field	97.8
J 7	Natural - Field	97.9
J 8	Natural - Field	99.4
Avg. Except J 1		98.9

Table 11

PERCENTAGE OF ALL IRON REMOVED BY THE SAND
FILTER, FOR VARIOUS WATERS

Water		Iron in Raw	Per Cent of Total Iron in Raw Water Removed
Group	Type	Water, mg/l	by Filter Only
A	Synthetic	5.1	50
B	Synthetic	3.3	72
C 1	Synthetic	4.5	65
C 2	Synthetic	3.1	88
D 1	Synthetic	3.2	85
D 2	Natural	4.5	80
D 3	Natural	4.5	69
D 4	Natural	3.9	78
E	Natural	5.1	75
F 1	Synthetic	2.3	94
F 2	Synthetic	2.9	97
G 1	Synthetic	3.2	85
G 2	Synthetic	5.3	52
H 1	Natural	2.3	78
H 2	Natural	2.8	63
J 1	Natural	17.9	0
J 2	Natural	16.4	67
J 3	Natural - Field	11.2	95
J 4	Natural - Field	11.4	92
J 5	Natural - Field	11.7	96
J 6	Natural - Field	11.2	98
J 7	Natural - Field	11.3	98
J 8	Natural - Field	11.4	98

Attempts to relate either percentage of iron removed, or iron re-maining in the effluent, to either final pH or the change in pH showed no corre-lation.

F. Effect of Variations in Sedimentation Time

The 6 field experiments, the J series, were designed to study the effect of variations in sedimentation time. The following times were used: Experiment No. 19, 75 minutes; No. 20, 60 minutes; No. 21, 90 minutes; No. 22, 30 minutes; No. 23, 0 minutes; No. 24, 30 minutes. For the detention times studied, overall efficiency and the efficiency of the various treatment units was apparently not affected. Iron removal efficiency remained high whether the sedimentation time was 90 minutes or zero.

During Experiment No. 23, where no sedimentation time was provided, a rapid build-up in headloss in the filter was noted. After the second hour of operation, the filter developed a negative head. From the analyses of water taken from the sample taps in the filter, it was noted that the iron steadily penetrated deeper into the filter. However, the removal of iron by the filter was 98 per cent which was about the same as that observed for the other experiments. After the completion of this experiment, a re-calibration of the flow rate revealed that it was 555 cc/min or 133 per cent of the design rate. This excess flow rate could possibly account for the rapid build-up in headloss.

G. Miscellaneous Determinations

The routine analysis of the waters provided data for some evaluations of the following parameters:

1. Alkalinity
2. Hardness
3. Total solids (residue)
4. Sulfates
5. Chlorides
6. Nitrogen and COD

1. Alkalinity

Table 12 summarizes iron removal in relation to the alkalinity changes for each experiment. Twelve of the 23 experiments showed an overall reduction of alkalinity, while the other 11 showed a small net gain or no change in alkalinity. For experiments 22 through 24 the increase in alkalinity after treatment was pos-sibly the result of a delay in analysis of from 24 to 48 hours after the samples

Table 12

RATIO OF ALKALINITY REDUCTION TO IRON REMOVAL

Water		Iron Removed mg/l	Alkalinity Change mg/l	Ratio Alkalinity Iron
Group	Type			
A	Synthetic	5.1	+1	Gain
B	Synthetic	3.42	-2	0.59
C 1	Synthetic	4.44	+3	Gain
C 2	Synthetic	3.10	-2	0.65
D 1	Synthetic	3.21	-4	1.25
D 2	Natural	4.51	-3	0.67
D 3	Natural	4.47	-4	0.89
D 4	Natural	3.92	-3	0.77
E	Natural	5.02	-9	1.80
F 1	Synthetic	2.30	0	----
F 2	Synthetic	2.88	Not available	----
G 1	Synthetic	3.18	-6	1.88
G 2	Synthetic	5.26	0	----
H 1	Natural	2.30	+4	Gain
H 2	Natural	2.69	+4	Gain
J 1	Natural	5.18	-4	0.78
J 2	Natural	16.35	-20	1.22
J 3	Natural - Field	11.16	-14	1.25
J 4	Natural - Field	11.11	-4	0.36
J 5	Natural - Field	11.45	-12	1.05
J 6	Natural - Field	10.90	+11	Gain
J 7	Natural - Field	11.06	+5	Gain
J 8	Natural - Field	11.32	+4	Gain

Mean Value   1.01

Expected Value, Reduction of Alkalinity for 1 mg/l Fe   1.78

were taken. The reduction of alkalinity per mg/l of iron removed showed a spread from 0.59 to 1.88 mg/l, as $CaCO_3$, with a mean value of 1.0 mg/l. Stoichiometrically, the reaction of oxidizing the iron bicarbonate predicts an alkalinity reduction of 1.78 mg/l for every mg/l of iron oxidized and removed. The experimental data thus indicated that only about 59 per cent of the expected alkalinity reduction occurred. The 59 per cent reduction is for the overall treatment, but occasional analysis of intermediate alkalinity values showed that almost the entire change in alkalinity took place after the aeration. On this basis, the percentage of expected alkalinity reduction was about the same as the percentage of the expected dissolved oxygen reduction--59 per cent and 50 per cent. This unexpected close agreement may be indicative of some removal mechanism which does not utilize dissolved oxygen and alkalinity.

2. Hardness

The hardness of the raw water which in this study varied from 253 mg/l to 427 mg/l has shown no effect on iron removal.

3. Total Solids

Data on the reductions of total solids were available only for the experiments conducted on the water having a high iron concentration. From 8 experiments on this water, it was found the mean total solids change was 22 mg/l, with a range from 2 to 45 mg/l. The mean iron reduction as iron was 11 mg/l; converted to iron hydroxide, and assuming the waters of hydration would be driven off, this reduction is equivalent to 19 mg/l of residue.

The agreement between the 22 mg/l observed difference and the 19 mg/l calculated difference seems significant, especially since the raw water carried some very fine silt, and the amount of silt seemed to vary from experiment to experiment.

4. Sulfate

Sulfate analyses showed no appreciable change in sulfate concentration between raw and finished water, either natural or synthetic. One exception was the experiments where sulfite was introduced as an oxygen scavenger to maintain a low raw water DO. This water showed a sulfate increase almost exactly as predicted from the sulfite added.

Both high and low sulfate waters were tested; both were equally satisfactory in iron removal.

5. Chloride

Chloride analyses of raw and finished waters showed occasional gains in chloride during the early stage of an experiment. This was due to carry over of HCl from the cleaning operation. There was no significant change of chloride with respect to iron removed, either with natural or synthetic waters. Both high and low chloride content waters were tested.

6. Nitrogen and COD

Table 13 gives a summary of the ammonia nitrogen (NH_3-N), organic nitrogen (Org.-N), and chemical oxygen demand (COD) analysis made on natural raw waters and some effluents.

It was found that the raw water total nitrogen (Total -N) concentration in no way affected the amount of iron removed, or the ease with which iron was removed from the experimental waters.

Determinations of nitrogen for both raw and finished water in the J series showed a 2.6 per cent reduction of the total nitrogen as a result of the iron removal treatment.

A relatively high COD was found in those waters which had a high Total-N concentration. The significant COD and nitrogen levels indicated that organic matter was present in some waters; and, for Experiments 12 plus 17 through 24, contamination by an Organic-N waste is suggested. The difference in the ratio of nitrogen to COD also suggests that the organic matter present differs from source to source, or that the COD was influenced by a variety of other oxygen consuming constituents.

Only the J series was analyzed for effluent COD; the change in COD was about 7.0 mg/l, or 13.2 per cent, representing an appreciable oxidation by the aeration unit.

Table 13

SUMMARY OF NITROGEN & COD DATA

Water		Nitrogen, mg/l						COD			
Group	Exp. No.	Raw Water			Finished Water			Raw mg/l	Fin. mg/l	Org. N COD	Tot. N COD
		NH_3-N	Org. N	Tot. N	NH_3-N	Org. N	Tot. N				
H 1	11	1.6	0.55	2.1	Na*	Na	---	Na	Na	Na	Na
E	12	16.7	0.50	17.2	Na	Na	---	32.9	Na	0.015	0.52
D 2	13	4.6	0.20	4.8	Na	Na	---	24.9	Na	0.008	0.19
D 3	14	5.6	0.20	5.8	Na	Na	---	10.0	Na	0.020	0.56
H 2	15	2.6	0.60	3.2	Na	Na	---	16.6	14.5	0.036	0.19
D 4	16	6.2	0.25	6.4	Na	Na	---	0	0	---	---
J 1	17	15.4	.90	16.3	Na	Na	---	52.0	46.7	0.018	0.31
J 2	18	15.6	1.10	16.7	Na	Na	---	50.1	46.7	0.022	0.33
J 3	19	14.4	1.05	15.4	14.2	0.95	15.2	Na	Na	---	---
J 4	20	14.2	0.68	14.9	14.2	0.72	14.9	Na	Na	---	---
J 5	21	14.2	1.03	15.2	Na	1.12	---	52.0	47.9	0.020	0.29
J 6	22	14.2	0.76	15.0	15.0	0.85	15.8	49.4	44.5	0.015	0.31
J 7	23	14.1	0.85	14.0	14.3	0.80	15.1	50.8	45.6	0.017	0.29
J 8	24	15.5	0.26	15.7	14.3	0.98	15.3	65.2	43.3	0.004	0.24

For Experiments 17-24, on water all from same source:

Parameter	Raw Water	Finished Water	Absolute Change	Per Cent Change
Mean NH_3 N mg/l	14.6	14.4	0.2	1.4
Mean Org. N mg/l	0.8	0.7	0.1	12.5
Mean Tot. N mg/l	15.5	15.1	0.4	2.6
Mean COD mg/l	52.8	45.8	7.0	13.2

*Not available.

IV DISCUSSION OF RESULTS

A. Preparation of Synthetic Ground Water

There are very few references available on how to prepare synthetic ground waters, or on how to accomplish economical carbonation and oxygen stripping which is important in preparing waters for studying iron removal. The most advantageous sequence of gas application seems to be carbonation, concurrent with filling the reservoir and with the compounds for alkalinity and hardness present. This may be followed by N_2 stripping, if necessary, to lower the DO to a concentration of about 0.10 mg/l prior to the addition of the ferrous compound. Since N_2 also strips out CO_2, and thus raises the pH, it is desirable to re-carbonate slightly after the stripping. Mixing during an experiment was accomplished by N_2 agitation; this resulted in gradual pH shift during the experiment.

Water characterized by alkalinity greater than hardness appears less stable; i.e., iron is more readily oxidized and removed. This observation agrees with the formulation of the reaction from ferrous bicarbonate to hydrated ferric oxides, in which bicarbonate is required to complete the reaction to a floc which will precipitate.

The observation that free CO_2 reduces the pH was in accord with the expected equilibria conditions; the waters prepared for laboratory experiments were generally buffered by the presence of other salts. The pH values for the more stable waters was in agreement with the pH of natural waters. The synthetic waters used in this study substantiate the concept that high CO_2 retards oxidation because the high CO_2 experimental waters were more stable and remained clear (unoxidized) for longer periods. This is true only for waters without organic complexing.

B. Aeration Unit and Dissolved Oxygen Study

The aeration device provided vigorous aeration, with long exposure of the water to the bubbles. The salt tracer technique was found to be a convenient means of measuring the detention time. Calculations based on the tracer study showed an effective recirculation of 1.5 times through the multiple-pass aerator and a detention time of 14 minutes. The aerator may have served as an upflow clarifier, as was shown. The ability of the experimental aerator to consistantly produce a water of about 80 per cent saturation, without regard to initial DO (as long as it is low) or mineral characteristics is an advantage not possessed by conventional aerators as reported in the literature. It should be remembered,

however, that the air rate used in the experimental studies is far in excess of any rate used in practice. Further study of the aeration ability at different air rates are to be made.

The overall decrease in DO through the reaction-sedimentation plus sand filtration processes was found to be sufficient to account for the oxidation of only 50 per cent of the total iron present after aeration, but removed from the finished water. Since the ferrous iron determinations positively showed ferrous iron present after aeration, the most plausible reason for the decrease in DO is that the DO was, in fact, used in the oxidation of the ferrous iron. This decrease in DO occurred mostly in the filter. There are three possible mechanisms which might contribute to the overall efficiency of iron removal: a) catalysis by previously deposited material in the filter; b) a very long passage and contact time with thin films, etc., which could promote the oxidation reaction; c) adsorption and reaction phenomena based on the adsorption of flocs to the sand grains and subsequently oxidation.

The catalytic effect of "ripened" filters is widely discussed in the literature; the other possibilities are not. The same sand was used throughout all experiments, so it is possible that the bed became "ripened".

The time of passage in the filter was actually quite short, since about two liters of water would fill all the voids. Two liters would represent a five minute flow-through time during which accelerated oxidation by tortous paths and close contact might be expected (postulate b). The oxidation and removal rate would then have to have been greatly accelerated, particularly since oxidation and removal in the reaction-sedimentation process was very slight for times of 30 to 90 minutes.

Vigorous backwashing after each experiment removed as much floc as possible from the filter, so that any floc adhering to the sand would have to be placed as an experiment progressed. The removal by adsorption would thus be expected to increase, as more flocs were deposited on the sand, or, therefore, as an experiment progressed.

The effluent usually showed an iron concentration greater during the first few hours of an experiment than during the remaining time, up to a definite break-through. This early higher concentration lends support to postulate c, that removal did proceed via an adsorption mechanism, and that the mechanism was more effective during the middle time period of an experiment.

It is also possible that the filter was not operating at peak iron removal until the first large flocs had been deposited on the top of the sand and thus created a micro strainer which was effective in trapping all subsequent flocs. A filling of pores in the upper sand layers was observed, but no real build up of floc deposit was noted.

C. Iron Removal

The consistantly high removal of iron from a variety of waters showed that none of the routinely determined mineral characteristics of the waters studied had any appreciable effect on the overall efficiency of iron removal by aeration, reaction-sedimentation, and sand filtration.

The one experiment which gave only 28 per cent removal of iron should not be completely discounted. The probable explanation of poor removal may be related to the fact that the water was taken from a well which had not been used for some time; the iron content as a result of standing was about 17 mg/l--much higher than for the other experiments. Subsequent experiments with this water gave satisfactory results. The conclusion drawn, then, is that the extremely high iron content, plus the possibility that the iron may have been of a different character either because the water was in contact with the well casing for some time, or because iron was actually picked up from the casing, accounts for the unsatisfactory removal performance.

Other experiments with water from the same source showed satisfactory removal, but the raw water iron content was less--about 12 mg/l, and the well was flushed before the water was collected. The use of a flocculator in Experiment 19 did not appreciably alter the removal by the reaction-sedimentation unit, but it may have improved the floc so that the iron was removed more efficiently by the filter.

In the aerator, removal is by two mechanisms: by adhesion of the ferric oxide to the surfaces of the aerator (especially noticed at the foam region of the center tube), and by sedimentation in the up-flow portion of the aerator. The diffuser in the aerator gradually clogged during an experiment, making it necessary to gradually increase the air pressure to maintain a steady flow. From this experience, it is believed that proper maintenance of diffusers would be very important to the successful operation of a plant using diffused air.

Iron removal by the reaction-sedimentation tank was consistantly small. Synthetic waters appeared to be more likely to form settleable floc. The waters with high sulfate concentrations show consistantly better removal by sedimentation, while the low sulfate waters occasionally showed some removal by sedimentation.

The natural samples brought to the laboratory showed very low iron removal by the reaction-sedimentation process. This may be correlated with the aeration device removal since it was shown that the aerator removed more iron from natural samples brought to the laboratory than from others, and that the removal was most probably by sedimentation in the aerator.

The field studies showed no iron removal in the reaction-sedimentation tank. Possibly this resulted from insufficient time to complete the oxidation, plus insufficient mixing and time for sedimentation to be effective.

Synthetic samples (which showed some sedimentation removal of iron) did not contain organic matter, so no complexing of the iron, or interference with coagulation would be expected for this reason. Jar tests showed that the typical fluffy, gelatinous flocs were formed with the synthetic waters; the typical flocs were not formed with most natural waters.

A separate experiment showed that a very long sedimentation time increased the percentage of iron removed. After one experiment was completed, the sedimentation tank supernatant was sampled without disturbing the small precipitate on the bottom. After 3 days of quiet sedimentation, the supernatant liquid was again tested for iron. The iron concentration of the supernatant decreased from about 11 mg/l to 0.1 mg/l.

In this experimental work, the sand filter accomplished most of the iron removal--50 to 98 per cent of the total amount removed for the waters tested. The balance of the removal was done by the aerator and the reaction-sedimentation unit. In experiment J 1 all iron removal took place prior to the filter. In all remaining experiments, the filter removed from 95 to 100 per cent of the applied iron, and averaged 98.9 per cent. There was no trend for separation of performance by water groups. It is noted in Table 10, however, that natural waters less frequently showed a 100 per cent removal of applied iron by the filter. This might be the result of organic complexing, since only the natural waters had organic matter present. Even at that, only the J series had much organic matter, as evidenced by a COD of about 50 mg/l, and this water showed a fair iron removal by the filter.

In this study, the iron concentration in the effluent followed a definite time oriented pattern; a typical plot is shown in Figure 10. The relatively high iron in the first hour or two indicated that iron passes all the way through the filter until some "adjustment" occurred. This "adjustment" took an hour or two, and might represent the time required for the collection of flocs on the surface of the filter, or time for individual grains of sand in the
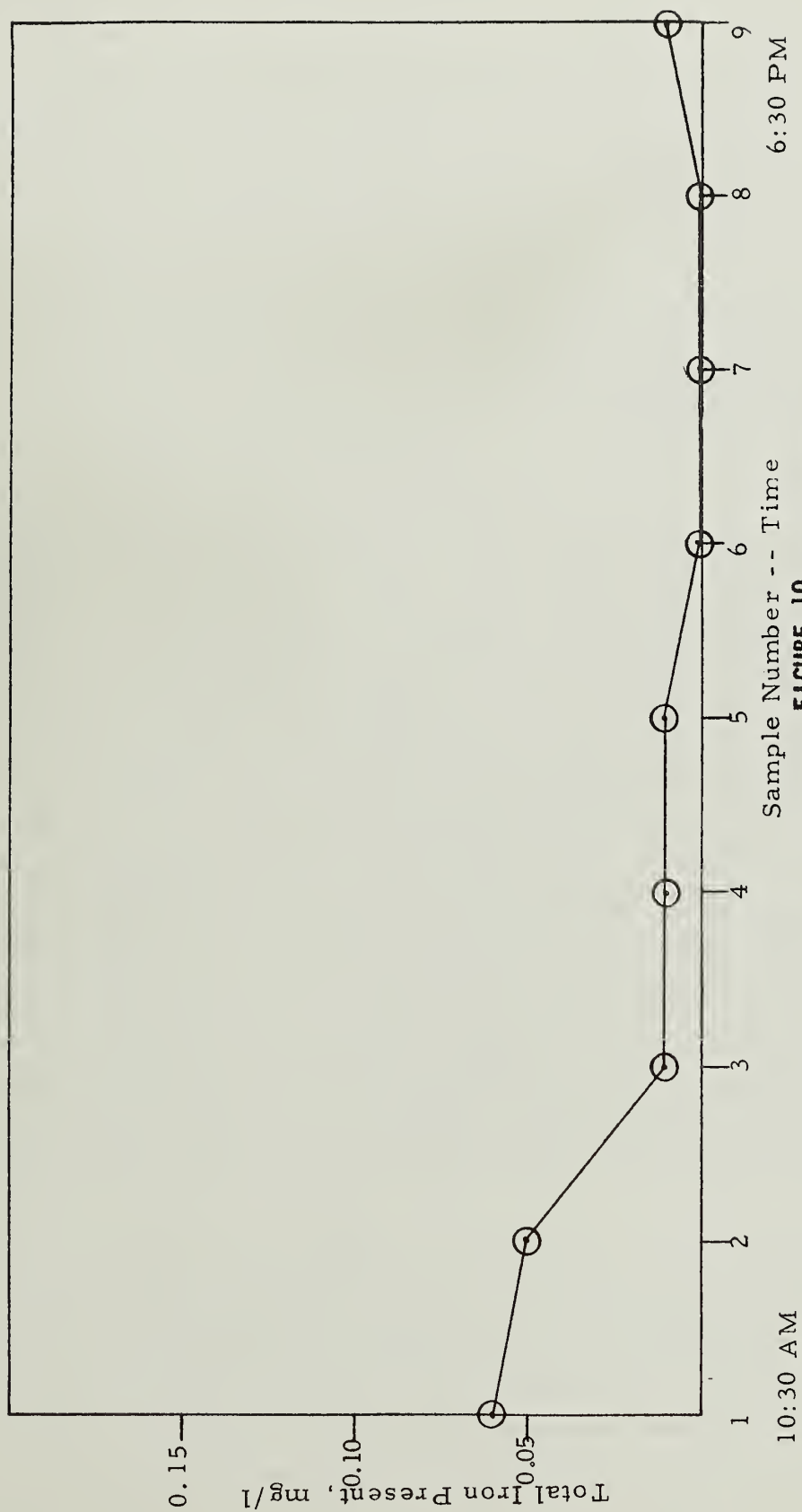
Sample Number -- Time

FIGURE 10

Natural Water Experiment 13
Plot of Effluent Iron Concentrations
Iron in Raw Water, 4.5 mg/l

interior to become coated and catalytically active. In view of the rather vigorous back washes used, and the absence of any well defined, visible surface deposits, it would seem that adsorption of the floc on the sand particles, and subsequent increased surface activity might be responsible for the improved removal of iron after a short time of operation. The upward trend of iron concentration at the end of an experiment resulted from break through of iron, most likely floc. Only in the long field runs with high iron was floc visible as turbidity in the effluent near the end of the run.

Occasional isolated occurrances of high iron concentrations (0.5 mg/l) were noted in effluent samples; these were too frequent to be dismissed as accidents, especially during the field studies. It is hypothesized that the iron was ferrous iron which was not oxidized.

D. Carbon Dioxide Reduction and pH Considerations

Carbon dioxide plays an important role in the mechanisms of putting iron into solution in ground waters. Most authors agree that the presence of CO_2 also hinders iron removal because it promotes a lower pH and because it tends to reverse the iron oxidation reaction in which free CO_2 is a product.

The results of this study indicated that the overall efficiency of iron removal from the waters studied was not noticeably influenced by the concentration of CO_2 in the raw water, the concentration of CO_2 remaining after aeration, or the percentage change in CO_2 resulting from aeration. The initial CO_2 concentration varied widely, yet the iron removal was uniformly 95 per cent or greater. The solubility of the ferric oxide hydrates depends on pH. Accordingly, the pH conditions also were studied for each experiment. Aeration, by stripping out CO_2, raised the pH of the waters approximately 0.63 units. Differences in pH changes among waters presumably were due to changes in concentration of CO_2, since no chemicals were added. The pH change, thus directly related to the CO_2 change, should be attributed to the same factors which controlled the CO_2.

The pH increases during reaction-sedimentation and filtration were slight but measurable, and could be the result of one or more of three actions.

a. Additional CO_2 removal from exposure during reaction-sedimentation.

b. Removal of CO_2 within the filter resulting from the decreased solubility of CO_2 in water under less than atmospheric pressure; the reduced pressure occurs as head loss in the filter increases.

c. Additional oxidation of ferrous iron, followed by CO_2 liberation and removal.

From the study to date, there appears to be no correlation between iron removal efficiency and pH or CO_2. This agrees with the literature inasmuch as the usual pH values for iron removal were met; it does not agree with the reports which claim the removal of iron is very sensitive to pH, unless this observation refers to pH values much lower than those found in the waters used in this study.

E. Miscellaneous Determinations

1. Alkalinity

The usual oxidation of ferrous bicarbonate, with the end products of H_2O and CO_2, would be expected to cause a net decrease in measurable alkalinity, if the ferric hydroxide was formed. Thirteen of the experiments showed a measurable decrease in alkalinity; however, there was no correlation with gross iron removal, either for natural or synthetic waters. The alkalinity, all as bicarbonate, was greater than the hardness in most waters.

2. Total Solids

The removal of iron which would make up part of the total solids would be expected to make the solids concentration in the effluent less than in the raw water. This effect was noticed, in about the ratio predicted if the iron removed is assumed to be ferric hydroxide. The total solids present had no apparent effect on the iron removal performance of any water.

3. Sulfates

If the removal of iron by the reaction-sedimentation process is assumed to include the effect of coagulation (a valid assumption for the apparatus), then the experimental work should indicate that there was improved coagulation with water having high sulfates. This was observed for iron removal since the high sulfate waters showed an average reduction of 7.8 per cent while the others showed 1.8 per cent reduction by sedimentation. The overall iron removal, however, was not appreciably changed.

4. Nitrogen and COD

Ammonia nitrogen is quite common in ground waters, and ranges from traces to 5 or 6 mg/l. The experimental waters were within this magnitude, except for the J series, which showed about 15 mg/l, NH_3-N. The organic nitrogen ranged from a trace to 1.1 mg/l. Complete data regarding the change in organic nitrogen is available only for the J series; it showed a definite, but small, reduction during treatment. This was possibly due to oxidation of organic matter.

Organic matter is believed to hinder the removal of iron from some

waters. Based on COD analysis, several waters showed some organic matter (COD from 10 to 30 mg/l--not unusual for well water) while the J series showed a high COD, about 51 mg/l. The J series contained one experiment which failed in iron removal, but the others were 95 to 97 per cent effective. In these cases, the organic matter did not seem to prevent satisfactory iron removal.

Treatment reduced the COD of the water used in the J series by 5.2 mg/l, or 11 per cent, while organic-N was reduced 0.1 mg/l or 12.5 per cent. If the organic nitrogen was all protein, the change represents oxidation of 0.7 mg/l protein. The presence of protein was reasonable, because the high total and organic nitrogens are reasonable indicators of contamination at some time by an organic waste.

The wide spread in values of organic nitrogen to COD indicated that the waters contained a variety of oxygen consuming constituents, not all of which are necessarily organic matter. The identification of organic matter in water, and the relationships between the organic matter and iron removal, as well as to treatment in general, is one of the most important aspects for future study.

5. Oxidation-Reduction Potential Measurements

The laboratory's battery-operated and line-operated ORP instruments have been checked against standard ORP solutions (Zobell's solution and quin-hydrone) and against various waters and have been found to give consistent results after an initial stabilization period of approximately 10 minutes. These instruments have also been checked against the instrument of the Illinois State Health Department and the values obtained by these instruments correlate very closely.

ORP measurements made during the J series field experiments indicate that ORP definitely changes from a minus value for raw water to a plus value for treated water.

V CONCLUSIONS

A. Design and Construction of Equipment

From a literature study of processes and equipment, a pilot plant for iron removal by aeration and filtration was designed, built and tested. The unit satisfactorily removed iron from a variety of natural and synthetic waters.

B. Special Techniques for Study

The experimental work has confirmed weaknesses in the following analytical techniques, as applied to water analysis:

1. The ferrous iron determination has not been satisfactorily developed for rapid and precise analysis of small concentrations in water.

2. The identification of trace organic matter in water supplies has not yet been developed to a reliable, easily performed determination.

Other mechanical and analytical problems related to operation of the pilot plant were satisfactorily resolved.

C. Preparation of Synthetic Ground Water

1. The choice of a compound to add iron to a synthetic water depends principally on the anionic qualities desired in the prepared water, and the solubility of the compound. Both ferrous chloride and ferrous sulfate were successfully used for the preparation of representative ground waters.

2. Both nitrogen and carbon dioxide gas were effective for removing dissolved oxygen, which is required in preparing waters representative of natural ground waters. Nitrogen was found to be slightly superior as a stripping gas.

3. Synthetic ground waters containing about 30 mg/l CO_2 were found to be stable for a short time; 100 mg/l CO_2 increased the stability of the ferrous iron. The most stable water was produced when CO_2 was applied last.

4. Waters with more alkalinity than hardness were less stable toward ferrous iron, and the iron was readily oxidized.

5. The sulfate concentration was of no significance in the stability of ferrous iron in synthetic ground waters.

6. The dissolved oxygen present when the iron compound was added was less significant in the stability of ferrous iron than was pH, CO_2

and alkalinity; however, low DO values were necessary to properly simulate ground waters.

7. In the range of pH values above 5.8, pH can be linearly correlated with ferrous iron stability, the alkaline waters being less stable than the acidic waters.

D. Results of Testing the Pilot Plant on Various Waters

1. The Aeration Unit and DO Study

a. The multiple pass aerator unit accomplished a vigorous aeration with a long contact time.

b. Some iron was removed during aeration as a result of sedimentation or adhesion to the equipment.

c. The final DO level, and the increase in per cent saturation of DO was rather uniform for all waters studied regardless of mineral characterization.

d. The DO change in the filter was related directly to the concentration of ferrous iron remaining after aeration; this appeared to depend, in turn, upon the character of the water.

2. Iron Removal

a. A 99 per cent reduction of iron in the experimental waters of varying character was accomplished.

b. The unit processes, by themselves, accomplished the following per cent reductions of iron:

Process	Per cent Reduction	
	Mean	Range
Aeration	25	4-44
Reaction-sedimentation	3	0-12
Sand Filtration	99	95-100

c. For the complete treatment system, the filter removed from 50 to 98 per cent of the total amount of iron removed. Of the total amount of iron removed, the filter was most effective with waters having a total hardness equal to or greater than the alkalinity. For waters with alkalinity in excess of hardness, the filter was responsible for slightly less of the total iron removed. The filter also removed a greater percentage of the total iron removed from natural waters, as compared to synthetic waters.

3. Carbon Dioxide and pH Study

a. The experimental aerator was efficient in removing CO_2, and therefore it was effective in raising the pH of the experimental

waters.

b. A linear correlation between percentage of CO_2 removal and in-
crease in pH was found; all waters fitted the correlation without
regard to source or characterization.

c. The stripping rate for CO_2 removal varied widely among the waters
and showed no correlation with mineral characterizations.

d. The final pH of the water, which was always above 7.4, showed
no correlation with net iron removal, nor with the percentage
reduction of iron.

4. Effects of Variations in Sedimentation Time

a. Variations in sedimentation time over the range studied had no
effect in overall treatment efficiency.

b. When sedimentation was eliminated, headloss in the filter built
up very rapidly necessitating shorter filter runs.

5. Miscellaneous Determinations

a. Alkalinity was slightly reduced by the pilot plant treatment
processes. High alkalinity favored oxidation of the ferrous
iron, but had no effect on the overall removal of the iron.

b. Hardness was not affected significantly by the iron removal
process nor did variations in hardness concentration have any
effect on iron removal.

c. The experimental treatment plant unit reduced the total solids
(residue) of both synthetic and natural waters by the predicted
amounts.

d. Waters with a high sulfate content showed better settling of
floc in the reaction-sedimentation process, but otherwise sul-
fate concentration was of no significance in iron removal. The
sulfate concentration was not altered by the experimental treat-
ment processes.

e. The chloride concentration was found to be of no significance in
iron removal; nor was it altered during treatment of the water.

f. The nitrogen concentrations, both ammonia and organic, were not
significant to the removal of iron by the pilot plant. Treat-
ment did slightly reduce the total nitrogen concentration of the
water. Chemical Oxygen Demand values varied widely with the
experimental waters, but no correlation with successful treat-
ment was found. A wide variation in the ratio of organic

nitrogen to COD indicated the presence of a variety of oxygen consuming compounds, none of which were identified by the routine chemical analyses performed.

VI PUBLICATIONS, STAFF AND FOREIGN TRAVEL

A. Publications

"Removal of Iron from Water by Aeration and Filtration", John M. Longley, M. S. Thesis, 160 pages, November, 1960.

B. Staff

R. S. Engelbrecht, Director - Time as required, February 1959 - to present.

G. E. Margrave, Assistant Director - Time as required, February 1959 - to present.

J. G. Weart, Consulting chemist - Time as required, February 1959 - to present.

J. J. Morgan, Engineer-in-charge - Quarter time, February 1959 - June 1959; Full time, July 1959 - September 1959; Quarter time, September 1959 - June 1960; Full time, July 1960 - September 1960.

J. M. Longley, Research Assistant - Half-time, February 1959 - June 1960; Full time, July 1960 - October 1960.

J. M. Moore, Research Assistant - Half time, July 1959 - June 1960.

L. R. Robinson, Jr., Research Assistant - Half time, February 1960 - to present.

K. K. Komolrit, Research Assistant - Half time, September 1960 - to present.

E. C. Reichelt, Chemist - Full time, September 1960 - to present.

C. Foreign Travel

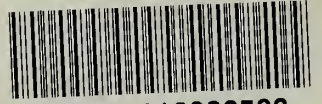There has been no foreign travel associated with this research grant.